Naval Research Laboratory

Washington, DC 20375-5320

Sea-based Fuel Synthesis Work at NRL from FY02 to FY07 (October 2001–October 2006)

DENNIS R. HARDY

Navy Technology Center for Safety and Survivability
Chemistry Division

August 5, 2010

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE *(DD-MM-YYYY)* 05-08-2010	2. REPORT TYPE Memorandum Report	3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Sea-based Fuel Synthesis Work at NRL from FY02 to FY07 (October 2001 – October 2006)	N00014
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
D.R. Hardy	61-T009-05
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER 61-9189-0-0-5

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Naval Research Laboratory, Code 6180 4555 Overlook Avenue, SW Washington, DC 20375-5320	NRL/MR/6180--10-9276

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR / MONITOR'S ACRONYM(S)
Office of Naval Research One Liberty Center 875 North Randolph Street, Suite 1425 Arlington, VA 22203	ONR
	11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This report includes the development of the core ideas behind the making of liquid hydrocarbons at sea from environmental sources such as carbon dioxide and water as early as the fall of 2001. It also details the formal NRL documents that established projects specifically dealing with this topic beginning in the spring of 2004. Finally, it includes some of the unpublished results of work done on recovering carbon dioxide from seawater as a source of carbon for fuel synthesis beginning in the fall of 2004. These results are interpreted in the light of current understanding of the total carbon burden of the ocean and the exchange over time between atmosphere and ocean. The status of the project as of the fall of 2006 and plans for 2007 are also included. All subsequent NRL work beginning in FY07 on this topic will be published separately in a timely fashion as it is completed.

15. SUBJECT TERMS

Seawater	Synthesis	Sea base
Liquid hydrocarbons	Carbon dioxide	

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Dennis R. Hardy
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	UL	52	19b. TELEPHONE NUMBER *(include area code)* (202) 767-2002

CONTENTS

SEA-BASED FUEL SYNTHESIS WORK AT NRL FROM FY02 TO FY07
(OCTOBER 2001 THROUGH OCTOBER 2006)

1.0   BRIEF HISTORY OF FUEL CHEMISTRY AT NRL AND EARLY
IDEAS OF USING ENVIRONMENTAL CO$_2$ TO MAKE FUEL

Fuel chemistry has been an integral part of the NRL Chemistry Division almost from the beginning [1]. As early as the mid 1930's there were programs on fuel combustion and investigations of other properties that were Navy shipboard unique such as water separation, microbiological growth contamination and accidental fuel fire extinguishment. Navy ships had switched from coal to black oil, also known as residual fuel oil, just after World War I. Aviation gasoline and early jet fuels began to be developed for potential aircraft carrier operations at the beginning of World War II. It became clear in the 1940s that the Navy would require a higher flash point aviation fuel than land based fuels either commercial or military, and this set the stage for continued investigation of this unique type of jet fuel in numerous other areas such as storage stability, high temperature stability, water coalescence, filtration, and low temperature performance at altitude.

Then in the 1970s the entire fleet of ships switched from black oil to a distillate fuel much like commercial diesel fuel. The exception to this was the submarine fleet and some aircraft carriers and a very small surface fleet of ships all of which were operated by nuclear energy. At about this time, the Arab Oil Embargoes took place and the NRL participated as a major player in the Navy led qualification of oil for both ships and planes derived from the vast US shale oil deposits, which were at that time owned by the Navy. This program spanned nearly a decade and involved every aspect of the development of a new liquid hydrocarbon from shale including mining, retorting, refining, performance evaluation, and compositional and property studies.

Navy fuel chemistry investigations continued in the last quarter of the twentieth century as global changes to the refining industry occurred which led to most jet and diesel fuel being much more highly processed in the refinery rather than simply straight run distillation operations that existed before the 1970s. The changes to fuels were many times very subtle and involved trace compositional differences that could lead to immense operations problems. Two examples were: (1) the storage stability of diesel fuels, where the refinery addition of cracked fractions that were **not** hydrotreated in an attempt to keep production costs low led to unstable fuels sometimes undergoing sludge formation a year or two after production, and (2) the hydrotreatment of jet fuel fractions that led to removal of beneficial surfactants and catastrophic fuel pump and fuel control failures in addition to loss of natural antioxidants preventing peroxide formation which could attack rubber o-rings in fuel systems.

The above problems arose from industry-wide refining changes over decades and usually led to more problems for the military fleet than the commercial fleet which did not store its fuels for more than 6 months before use. In addition to the above refinery problems which usually led to more problems for the military fleet than the commercial fleet, the ship and aircraft engines and fuel systems themselves continued to evolve and become more fuel efficient. This usually resulted in operating systems that were much hotter than earlier designs and this led to more potential problems from trace components in the fuels.

As the twentieth century drew to a close it became evident that the massive supply of cheap crude oil could be coming to an end, possibly as early as the first quarter of the 21st century. Although a very difficult thing to predict, many people both inside and outside the military began to investigate this potential problem. A similar problem had been investigated by the NRL in the 1970s but at that time the problem was not a global loss of cheap crude oil but just a US loss of such supply. Many of the findings and results of this exhaustive NRL 1974 study [2] remain valid even now for the Navy. Several at NRL began to push for an updating of the 1974 energy study near the end of the 1990s. Homer Carhart, instrumental in the production of the 1974 NRL report, and Burton Hurdle, the former superintendent of the NRL Acoustics Division, enlisted the assistance of Fred Saalfeld, former superintendent of the NRL Chemistry Division and former Director of Office of Naval Research, and Tim Coffey, former Director of Research at NRL, to convince VADM Paul Gaffney, former NRL CO, former CNR and then President of National Defense University (NDU), to sponsor a high level two day workshop to investigate the question of future DOD energy resources. ADM Gaffney then tapped Bhakta Rath, Associate Director of Research at NRL and Dennis Hardy, a long time NRL fuel chemist to actually convene the workshop with the assistance of Rich Carlin at Office of Naval Research.

Before the workshop was actually held at NDU in December of 2002 (one day) and May of 2003 (one day) there were almost weekly organizational meetings beginning early in 2002. Prior to this activity, however, and leading up to it, one of the topics from the NRL 1974 energy research report had been documented in an excellent book by William Avery of Johns Hopkins Applied Physics Lab and Chih Wu of the US Naval Academy, published in 1994. This book [3], *Renewable Energy from the Ocean, A Guide to OTEC*, described the DOE led effort in the late 1970s and 80s to develop closed cycle ocean thermal energy conversion to electricity. Two plant ships were actually evaluated and discussed in the book, a 40 kW vessel and a 1 MW vessel. Both produced electricity at the target levels, but neither actually produced any net energy. This was attributed to the fact that systems had not been optimized to work as a unit and the fact that scaling to such low levels of power production just to demonstrate the concept does not allow the possibility of net energy production.

The book essentially documents the real possibility of closed OTEC cycles producing large net power on the order of 100 to 200 MW, but not on an economically feasible ship or floating platform. Further, the problem of transmitting this fossil fuel free electricity to land greatly reduces the operating range of the process which is already limited to a band 15° north and south of the equator at ocean depths of at least 1000 m. In an effort to justify the OTEC work, the authors speculated on the ability of this electricity to produce a useful fuel or other product, which could be economically transmitted to land. One of the most interesting speculations was the production of methanol. This would arise from the use of OTEC generated

electricity to electrolyze water to produce hydrogen and the transport of coal to the OTEC ship as a source of carbon. These would be combined in the well know catalytic Lurgi process which is exothermic and has excellent industrial scale yields. Coal would be burned and the entire CO_2 produced would be reacted over copper oxide catalysts with the electrolytically produced hydrogen to form methanol and fresh water [3].

Although the Navy might be interested in making a liquid hydrocarbon by such a process in the middle of the tropical ocean, the scheme failed on three very important points. First, the use of coal as a carbon source in the ocean requires the transfer of coal great distances at sea and it would be energetically better to just burn the coal – back to pre-WW I. Second, the production of methanol with its extremely low flash point of about 11 ºC presents an insurmountable safety issue for fire at sea, especially for the Navy. Third, the volumetric energy content of methanol is so much lower (roughly half) than petroleum derived jet fuel that this would also not be possible for naval aviation mission use. Near the very end of the book is a discussion of the potential drawbacks to the OTEC closed cycle process itself, and although the discussion contained errors about the actual concentration of carbon dioxide in seawater, the production of CO_2 (as a byproduct of the process) which is vented to the atmosphere from the cold seawater pumped to the surface presents a formidable challenge. Avery, a physicist, and Wu, a mechanical engineer, did not jump on the idea that this very CO_2 degassing from the ocean might be a potential source of enough carbon already at the ship to use as a source of making hydrocarbons.

During discussions in the summer of 2001, Mike Rigdon, of the Institute for Defense Analysis (IDA), and Dennis Hardy at the NRL began to do the calculations that seemed to support the idea of using CO_2 and hydrogen at sea in a polymerization process similar to a gas liquid catalysis process such as traditional Fischer Tropsch to produce liquid hydrocarbons (and fresh water in equal volumes), all on a shipboard platform. It was about this time that the Sea Basing concept at ONR was being proposed as a Future Naval Capability, but there was no interest in changing the business as usual (BAU) scenario for fuel procurement within the Navy. Thus a proposal was drafted by Rigdon and Hardy presented to Robert Nowak of DARPA with the intention of holding a series of workshops to identify scientific concepts, any technological barriers, the overall feasibility of the idea, and a rudimentary first look at the economics of the process when compared to current BAU.

Although Nowak was initially skeptical, he was not unfavorable to the idea of the workshops. Unfortunately, he retired soon after the initial meetings and no one else at DARPA could be identified as a possible sponsor of the workshops. The scheme that Rigdon and Hardy first envisioned was the shipboard production of about 100,000 gallons per day of liquid hydrocarbon similar to jet fuel. This would be about the daily average consumption of a typical aircraft carrier. Although calculations had indeed shown that OTEC appeared to be a viable source of all 3 necessary components, electricity, hydrogen, and CO_2, this early proposal to DARPA would also determine if existing shipboard nuclear energy sources could provide sufficient electricity to produce the necessary hydrogen to make liquid hydrocarbons at the planned target rate. Because the initial full scale numbers appeared to overwhelm people, Rigdon and Hardy reduced the proposed planned target to only 10,000 gallons per day, or about 10% of typical daily aircraft carrier jet fuel use during peacetime operations.

Hardy had done the original calculations, which will be described below in detail, and these showed that there was more than enough CO_2 available (as total CO_2 = carbonate + bicarbonate + dissolved CO_2 gas) in the volume of seawater needed to produce 100 MW of OTEC electricity to make 100,000 gallons per day of hydrocarbon, provided that at least 33% of the total CO_2 could be recovered. However, 100 MW of electricity was not enough in the worst case scenario to produce enough hydrogen so that all of the hydrogen and CO_2 produced every day would be consumed every day to produce 100,000 gallons of hydrocarbon per day, the typical average peacetime carrier use. For 100,000 gallons of fuel per day it would be necessary to produce about 160 MW of electricity. This was another reason that Rigdon and Hardy reduced the original DARPA proposal to 10,000 gallons of fuel per day. However, the 3 separate systems seemed to have almost the right balance to act in concert together without the need for any additional supplemental processes. This serendipitous fact was incredible. It meant that Avery and Wu had potentially been sitting in a sea of carbon and hadn't realized it.

Hardy and Rigdon took their proposal to DARPA in October 2001 (100,000 gallons of fuel per day) and again in January 2002 (10,000 gallons of fuel per day), but Nowak retired in the summer of 2002 without acting on the proposal for a DARPA workshop. At that time ADM Gaffney, then President of NDU, was approached by Hardy in July 2002, with the DARPA proposal in order to assess whether there could be any Navy interest in supporting this idea. The groundwork for the naval need for such projects had still not been adequately laid and ADM Gaffney was not just skeptical of the proposal, but more importantly, he was skeptical of the **need** for such a proposal at that time. Thus the stage was set to try to provide both the military need, through holding the NDU workshop of future energy resources beginning in late 2002, but also the stage was set for more detailed calculations of the process itself in order to provide a stronger proposal. This latter work was used to draft a proposal for NRL internal funding of some of the science issues that needed addressing. But that proposal was not even sent forward out of the Chemistry Division for similar reasons of skepticism about the naval need and the perception that the science issues involved were trivial. These latter science issues will be revisited in Section 17.1 below, while attempting to draw together some of the findings detailed in Sections 9.0 and 14.0 and basic science issues that have provided key direction to the future of the project.

In this report spanning FY02 (October 2001) to FY07 (March 2007), the DARPA proposal above is designated the "first" one since this was the first of three attempts during this period to interest DARPA in this topic. As indicated, this first DARPA proposal was to host a workshop to explore the scientific, technical, engineering, economic and other issues of this particular idea. The second DARPA proposal will be discussed in detail in Section 7.0 and was developed in 2004 with the ultimate goal of designing a pilot plant for the process. The third DARPA proposal was in 2007 and involved a second attempt to design the components necessary for a pilot plant. This third DARPA proposal will be discussed in Section 17.0.

The actual mass and energy balances necessary for a full scale nuclear powered system (as opposed to an OTEC system for electricity) to make 100,000 gallons per day of jet fuel out of hydrogen and carbon dioxide was part of this third DARPA proposal. However, the many questions relating to the different possible methods of hydrogen production and carbon dioxide reduction led to a variety of answers on the final electrical power requirements of the overall

4

process. These questions were removed from the third DARPA proposal, but an energy balance based on the worst case water electrolysis and total carbon dioxide reduction with hydrogen was assumed.

The original calculation of mass and energy requirements for this process was made in November 2002, just before the first NDU/ONR sponsored workshop on future DOD energy needs [4]. If we first assume an OTEC rather than a nuclear source of electricity, we need to specify the volume of water that is pumped to achieve a given power rating. The designs of Avery and Wu that were actually built to achieve a power rating of 40 MW pumped about 136,000 L/sec (roughly 36,000 gal/sec) of cold water. The warm water flow rate was not reported but it is typically about 1.6 times the cold water flow rate. This would give a total flow rate of about 354,000 L/sec (about 93,000 gal/sec) and to achieve 100 MW this flow total flow would be about 2.5 times the rate to achieve 40 MW. This would be a total flow rate of 885,000 L/sec (about 234,000 gal/sec).

For the much greater efficiency design of OTEC reported by Nicholson at the NDU/ONR future energy workshop [4] these flow rates to achieve 100 MW rating are less than half. Nicholson's design has not yet been built full scale, but component tests allow him to state that total flow would be 372,000 L/sec (about 98,000 gal/sec). Even when this lower flow rate is used, we can calculate that if the total carbon dioxide could be recovered this would amount to over 3,000 metric tons (MT) per day. The carbon requirement to make 100,000 gal/day of jet fuel with an average carbon number of 11 would be only about 880 MT per day. This means that we would only need to recover 28% of the total carbon dioxide from the OTEC process.

We next estimate that we would need to produce about 124 metric tons (MT) of hydrogen (H_2) per day for the full scale 100,000 gal/day scenario. In the initial DARPA proposal of Rigdon and Hardy only the hydrogen needed to actually react with carbon monoxide to form fuel and water was used. By the time of the second DARPA proposal, the additional hydrogen needed to reduce carbon dioxide was included. The 124 MT of hydrogen per day estimate above is a worst case estimate that requires the maximum amount of hydrogen from electrolysis processes at about 30 ºC. This amounts to about 1,374,000 cubic meters of H_2 per day.

If we use typical industrial scale water electrolyzers to produce our hydrogen, this makes the electrical burden about 4.2 kW/cubic meter or about 48 kW/kg of H_2. This computes to a worst case electrical requirement of about 240 MW for 100,000 gal/day of fuel production. The original calculation which disregarded any hydrogen requirement for reducing carbon dioxide was only about 65% of this number or just under 160 MW. Since the direct catalytic reduction of carbon dioxide by hydrogen and the production of hydrocarbons is still the subject of intense investigation and with many unknowns, we can estimate that 160 MW would now be a lower limit that we can attempt to achieve in future work. This will be discussed in more detail in Sections 4.0 and 10.0. From the above analysis it can easily be seen that the limiting factor in the entire scheme will be the electrical power needed to produce the required hydrogen. This same limitation holds regardless of electrical power source – OTEC or nuclear.

To summarize the original first DARPA calculations, we note that all 3 processes seemed to be in reasonable balance except that there is significantly more carbon available than needed.

During the actual NDU/ONR workshop on future energy needs for DOD [4] and the ensuing discussions, two conclusions were apparent. The first was that OTEC was the best possible source of future energy extraction of any of the ocean processes available, including waves, tides, and currents. The second conclusion was that there did not appear to be any impediments to designing a Navy led R&D program to investigate the science and technology issues of a sea based process to make fuel and that is the subject of the next 5 sections of this report.

2.0   NRL INVENTION DISCLOSURE AS THE FIRST FORMAL WRITTEN DOCUMENTATION

Because the first DARPA proposal was not finally put forward it was not formally documented. However, after detailed discussions with a number of people including those at IDA, NRL, DOE, and DARPA it became obvious that due to the potential merit of the actual idea it would be prudent to file a record and disclosure of invention as the first step toward filing for a patent. This was submitted on 10 February 2003 and the disclosure was assigned a Navy Case number 84,538.

The original disclosure was aimed entirely at an ocean based process that was envisioned as a future non combatant naval vessel which would generate its electrical needs from OTEC. Although air was included as a potential source of carbon dioxide, the primary source was to be the much higher concentration available in seawater. In the summer of 2003 Tim Coffey suggested that the original disclosure be amended to include the use of nuclear and thermal energy as potential alternatives to OTEC electricity. At that point he was listed as a co-inventor on the disclosure and eventually on the US Patent.

No action was taken on this disclosure until April of 2004 when the NRL DOR, John Montgomery became actively interested in the project and asked that a patent application be filed immediately. This was done by Rebecca Forman of the NRL IP office and submitted as a US Patent application in April 2004. In November of 2004 an international patent was filed. The US Patent was granted on 2 September 2008 with patent number 7,420,004.

It should be noted that the overall performance of the process as described in the final patent details is for the best possible outcome. The patent indicated that up to 100,000 gallons of liquid hydrocarbon fuel per day could be produced by a large shipboard process by as little as 100 MW of power required. However, this would only be accomplished by the use of high temperature gas turbine (HTGT) nuclear reactors, which although now available commercially, have never been constructed at the required power levels of 100 to 200 MW. For the most likely naval nuclear vessel option on aircraft carriers the limitation for 100 MW would be between 40,000 and 50,000 gallons per day. For the next most likely commercial OTEC vessel with 100 MW available, the same volume limitation would apply. The OTEC design is considering the use of new generators capable of doubling the output of current generator designs and this would increase the OTEC output to between 80,000 and 100,000 gallons of fuel per day. The possibility of even higher outputs per electrical power inputs is possible by such future design combinations as the HTGT nuclear reactor with the new design for OTEC generators, but this is the subject of future ship designs. An example is given in Section 17.2.

3.0 DEVELOP   MENT OF INDUSTRIAL PARTNERS FOR THE PROJECT

In early 2003 the Navy received a number of requests to reevaluate hydrogen as a fuel for DOD. One response that was generated by National Defense University built upon the last major evaluation of hydrogen as a Navy fuel made by Carhart, et al. [5] in 1974. Coffey, et al. [6] reached essentially the same conclusions as the previous report of almost 30 years before. This was that hydrogen was not viable as a fuel for most DOD missions because of the requirement for compact, high volumetric energy density power. The report concluded that the DOD would likely have to increase its dependence on nuclear power and should also support R&D to investigate ways to utilize hydrogen by synthesizing hydrocarbon fuels in an environmentally compliant fashion.

In the writing of this report the 3 Navy authors were joined by 3 scientists from General Atomics in order to incorporate the contribution of nuclear energy into the mix of hydrogen production methods. General Atomics had been the primary developer of thermochemical cycles that produced hydrogen under very favorable economics and at the same time did not contribute to carbon dioxide production in the process in the 1970s. Of course the least expensive industrially used method of hydrogen production is steam reforming of methane, but this does not count the cost of carbon mitigation. The next most economic scheme is thermochemical cycles utilizing a HTGT nuclear reactor for the heat energy necessary for the sulfur-iodide cycle. This cycle produces absolutely no carbon dioxide, although it is about 70% more expensive than steam reforming per kg of hydrogen produced.

At the end of this report the possibility of storing the potential combustion energy of hydrogen as a synthesized hydrocarbon, much as nature as always done it, is suggested. The process that was disclosed in Section 2.0 above was used as an example of how shipboard production of hydrogen could thus be utilized to make hydrocarbons simply by using existing commercial water electrolyzers. The primary hurdle for this example at that time was the ability to obtain sufficient carbon from the air or ocean. The next biggest hurdle would be the generation of enough power to produce enough hydrogen to synthesize the required hydrocarbon fuel each day. The OTEC process was mentioned as a possible supplement for nuclear energy from currently used naval light water reactors.

It is interesting that in this paper [6] the first questions about the nature of the process in regard to the carbon dioxide rate of return from burning a hydrocarbon that had been made by removing carbon dioxide from the sea were posed. Would the rate of return from the atmosphere to the sea be fast enough to actually make this synthetic hydrocarbon scheme carbon neutral in regard to the atmosphere? The partial answer to this question will be addressed in Section 8.0 below, with a fuller answer hypothesized in Sections 17.1 and 17.2.

As a result of the collaborations in the writing of this paper which was published in November 2003, General Atomics approached NRL formally the following spring of 2004 with a proposal to work together on the issues raised on synthetic hydrocarbon production from nuclear sources for military use on a shipboard platform. That will be discussed in Section 5.0 below.

4.0   LITERATURE SEARCH ON FISCHER TROPSCH PROCESSES

After the publication of the NDU report on hydrogen as a DOD fuel in late 2003 the NRL DOR, John Montgomery, became interested in the topic of producing fuel from environmental sources on a shipboard platform. At that time the real question was whether or not there was any indication in the literature that even if sufficient carbon dioxide and hydrogen were available, that the catalytic chemistry would be favorable to produce the hydrocarbon products at the desired molecular weight range. Montgomery provided funding for a one month literature search to Hardy in March 2004 in an attempt to exhaustively search the last 80 years for guidance on this question. The literature search was completed with the assistance of Carol Lucke from the NRL library and reported to Dr. Montgomery in April of 2004. At that time a written report of the presentation was not made and it is now included as part of this report.

The presentation was in 5 parts. First, a report of the actual literature reviewed for this search, then a background tutorial for Fischer Tropsch Synthesis (FTS or FT), then a review of the water gas shift reaction, then a list of potential catalyst types, and finally a brief plan of future efforts following the presentation.

Seven major data bases were searched covering a time frame of about 1926 to 2004. First standard internet searches were conducted using typical search engines. Then 3 specific Fischer Tropsch (FT) archives were searched including the Department of Energy (DOE) FT reports, the Bureau of Mines (BOM) reports, and the German WWII reports. Next, the National Academy of Sciences (NAS) publications were searched and finally the specialized SciFinder search engine was used to do a complete Chemical Abstracts (CA) patent search and a CA search.

The CA search alone found about 1,400 references and patents from 1928. These were arranged into decades to produce the following interesting chart:

Years	# of References	Comments
1926-1940	A few	Inception of idea was mid 1920s
1941-1950	80	High number of Japanese papers
1951-1960	70	
1961-1970	30	
1971-1980	70	Mainly US
1981-1990	300	Mainly US
1991-2000	450	Mainly US
2001-2004	400	High number of Chinese papers

It is clear from this chart that from the beginning in Germany the actual publication of reports was interrupted by WWII. This becomes even more interesting when the post WWII reports from the BOM clearly indicate that the development of a major industry before and during WWII inside of Germany resulted in the production of fuel that allowed the continuation

of the war two years beyond what would have been possible without this in-country fuel making industry. The German concept of the so called Fischer Tropsch synthesis of hydrocarbons started with coal which was steam reformed to CO and hydrogen and then immediately fed into fixed bed reactors that operated using iron catalysts, one of the simplest and most basic processes possible. Germany had large reserves of coal but essentially no oil reserves internally.

As the petroleum industry was just getting underway after WWII there was still sufficient interest especially in completely energy poor Japan about the FT process as a possible source of indigenous fuel using Japanese natural gas as a feedstock instead of coal which was not available in Japan. Clearly the Japanese along with the rest of the world chose to go the simplest route possible which meant that FT easily lost out to petroleum refining. We see a clear trend with papers dropping in the 1950s and 1960s. Then during the politically motivated Arab oil embargo in the US, we see in the 1970s a renewed interest in FT and a clear shift in that interest to the US. Even in the 1980s and 1990s we see greatly increasing interest in the FT process but this is mainly because of basic science issues and the founding of the DOE in the late 1970s which encouraged FT along with many other traditional alternative schemes. In this first decade of the 21st century it looks like there will be at least a doubling in the number of papers on FT synthesis from the last decade of the 20th century. Here there is also no surprise that the interest has again shifted away from the US to China whose booming economy dictates the utilization of all sources of energy including FT from the massive coal resources of that country. Interest in FT in the US has waned due to the increased awareness of the adverse environmental effects of using coal as a starting material and the fact that US natural gas supply is rapidly depleting. The concern about environmental issues in China is clearly overshadowed by the energy pressures in that country.

In order to bring Dr. Montgomery up to speed regarding the whole history of FT synthesis of hydrocarbon liquids, a brief tutorial was assembled which was sensitive to the historical aspects as well as the chemistry aspects of this topic. What this means is that one needs to start at the very beginning of the FT process which means that in the traditional sense we must start with a fossil fuel such as coal or gas and use partial oxidation to form the products of carbon monoxide and hydrogen gases. These reactions called the synthesis gas reactions actually date from the early 1800s in the US. This mixture of carbon monoxide and hydrogen (called synthesis gas) was piped into homes as a source of heat and light when the mixture was combusted. The four reactions listed below require no catalyst. Although it is not included in the reactions, a significant amount of ash and carbon dioxide are usually generated in the formation of the synthesis gas. CH denotes the approximate molecular structure of coal.

Steam oxidation of coal: $CH + H_2O = CO + 3/2\ H_2$ (1)

Partial oxidation of coal: $CH + \frac{1}{2}\ O_2 = CO + \frac{1}{2}\ H_2$ (2)

Steam oxidation of methane: $CH_4 + H_2O = CO + 3\ H_2$ (3)

Partial oxidation of methane: $CH_4 + \frac{1}{2}\ O_2 = CO + 2\ H_2$ (4)
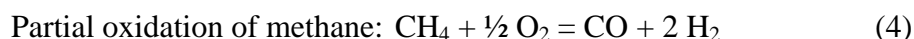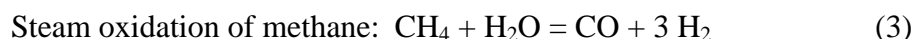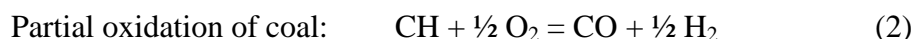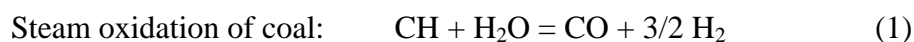
The first two reactions were the ones originally used in the US in the early 19th century and then by the Germans in the 1930s and 1940s, and most recently by the South African company SASOL in the 1970s until the present. Of course, only the Germans and South Africans used the synthesis gas as a feed to the catalytic FT synthesis reactions.

The third and fourth reactions have been used by the petroleum industry extensively since about the 1970s to the present in order to provide cheap hydrogen for upgrading poor quality petroleum products. For the last 20 years these two reactions have also been used to support the large tar sands liquid upgrading in Canada. However, there have been several attempts to utilize natural gas reforming (which is the name of these synthesis gas reactions) as a feedstock to FT synthesis. This approach under Army funded work in the last 10 years has proved very successful in forming high yields of military jet fuel.

The next step in producing hydrocarbons in this process is the FT synthesis reaction that uses synthesis gas as reactants and which gives the products of liquid hydrocarbon and water in equal volumes depending on the catalyst system used. A specific balanced example equation is shown for high flash n-decane:

$$CO + 2n \ H_2 = (CH2)_n + H_2O \quad \text{(for catalysts, see below)} \qquad (5)$$

$$10 \ CO + 21 \ H_2 = C_{10}H_{22} + 10 \ H_2O \qquad (6)$$
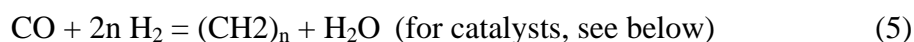
A major competing reaction as these progress to completion via free radical initiation, chain branching and termination steps is the so-called water gas shift (WGS) reaction. The product water begins to react with the reactant CO to form CO_2 and H_2 (a potential reactant in equation (6).

$$H_2O + CO = CO_2 + H_2 \qquad (K_{eq} = \text{about 1}) \qquad (7)$$
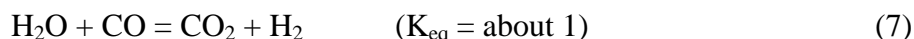
The reverse of this reaction is called the reverse water gas shift (RWGS) reaction. Note that the RWGS reaction is the current scheme's **starting materials or reactants.** Although this reaction can proceed without the use of a catalyst in either direction, the RWGS can actually be potentially enhanced by the use of catalysts. Because at equilibrium reaction (7) is balanced it is quite possible to selectively choose catalyst systems and conditions to produce water and CO. The CO then becomes the reactant in a traditional FT synthesis reaction, equations (5) and (6) and the hydrogen for the FT synthesis is provided by the electrolysis (or thermolysis, or both) of water.

If we also start with carbon dioxide and hydrogen from environmental sources and produce both of these potential reactants separately, we have the chemical luxury of blending them in any stoichoimetric ratio we desire and we have the technological luxury of blending them at different rates and at different positions in the reactor streams. Thus the stage seems set to determine a whole new series of reaction processes to directly utilize carbon dioxide and hydrogen in a new chain branching, catalytic scheme to produce the required hydrocarbon liquid.

One additional important thing to note is that reactions (5) and (6) do not give individual hydrocarbon products as shown in the example but a range of products is produced usually as normal and methyl branched hydrocarbons. The control of chain length and branching using traditional FT synthesis processes is reasonably well understood at this time.

A competing, alternative reaction that can take place under copper oxide catalysts with carbon dioxide and hydrogen, the well known Carnol or Lurgi process:

$$CO_2 + 3 H_2 = CH_3OH + H_2O \qquad\qquad (8)$$

Methanol can also be a potential source of carbon in the FT reaction, thus:

$$20 CH_3OH + H_2 = C_{10}H_{22} + 10 H_2O \qquad\qquad (9)$$
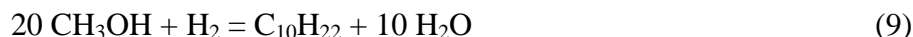
Thus both reactions, RWGS and Lurgi, can be used to drive the reactants available at sea to the desired products. The third part of the literature review focused on the importance of the RWGS reaction and conditions and how this becomes a key to the entire scheme of hydrocarbon synthesis. All gas to liquid hydrocarbon work done since the 1920s until the present involve fossil fuels to produce the synthesis gas. The next step of the process developed by Sabatier, Fischer and Tropsch involves the production of a series of increasingly higher molecular weight hydrocarbons. Through judicious selection of catalyst and process conditions, a wide variety of hydrocarbon types can be produced but water is always a major product of this process. Two things should be noted here. First, the present scheme does not start with any fossil fuel. Second, the proposed scheme can now make use of two other modes of chain branching, one leading to oxygen instead of water as the product and one leading to incorporation of some of the oxygen in the hydrocarbon portion of the products. Both of these last goals will make the process much less energy intensive due to the reduction in needed hydrogen by lessening the amount of water formed.

The fourth part of the review listed the potential catalyst types for gas to liquid and RWG reactions identified to date. These included almost every imaginable type of material including metals such as iron, cobalt and nickel; metal oxides of iron, cobalt and nickel plus some more exotic metals such as ruthenium; mixed metals of these; mixed metal oxides of these; alumina, zirconia, or other support type materials; and metals or metal oxides or mixed metals or mixed metal oxides on these supports. An example of a typical catalyst for the Lurgi process to make methanol would be supported Cu-Mn oxide or Cu-Zn oxide.

Most of these catalyst materials are not proprietary due to the long history of these processes. The RWGS reaction may be accomplished with or without the catalysts mentioned above. Equally important to catalyst selection is the definition of the actual process and its conditions. Chemically the best catalysts to date have tended to be the simplest, least expensive and well defined. Continued improvement of catalysts tends to be one of the perennial major efforts in FT work. The present scheme will focus not on improved catalysts but on actually changing the free radical chemistry mechanisms to minimize the production of water as a product.

At the conclusion of the review a somewhat more detailed literature search with an additional month of effort was recommended by Hardy. Dr. Montgomery also recommended that a patent application of the process be made to protect NRL and Navy interests and that commercial partners be sought out to make joint, full proposals to DARPA and ONR. The patent application described in Section 2.0 was a direct result of this literature review to Dr. Montgomery. The development of other government and industrial partners in this topical area is covered in Sections 5.0 and 6.0.

5.0   DEVELOPMENT OF THE NRL/GENERAL ATOMICS CRADA

In addition to the patent application that the NRL Director of Research (DOR), Dr. John Montgomery, requested in April 2004, he also encouraged Hardy to try to establish industrial partners via a Navy cooperative research and development agreement (CRADA). This was made simple when Dr. Ken Schultz, a co-author on the DOD Hydrogen paper [6] approached Hardy in that same month with the same request on behalf of his company, General Atomics. NRL strategic planner, Dr. Jill Dahlburg, NRL Code 1006, was also a co-author on this paper and she and Hardy contacted the NRL Technology Transfer Office to begin negotiations with General Atomics on a CRADA.

The interest of General Atomics (GA) was two fold. First, they were interested in trying to use nuclear energy, specifically high temperature helium gas cooled reactors as one potential source of very inexpensive hydrogen needed in the shipboard fuel making scheme. Second, they were interested in the sulfur iodide (SI) thermochemical cycle as an alternative source of very cheap hydrogen without the use of fossil fuel input. GA looked on thermochemical SI cycle as a possible bridging technology that could be energetically more favorable than simple commercial water electrolyzers. NRL came to the table with expertise in the needed fuel to be made and in the actual catalytic and other chemical processes that could be tailored for shipboard use. In addition NRL was already beginning the first experiments on extracting CO_2 from seawater.

During May and June of 2004 a Statement of Work (SOW) was developed and submitted to NRL Code 1004 for inclusion into the formal CRADA agreement. This agreement was signed by GA and NRL in July 2004 as NCRADA-NRL-04-350 entitled Development of Systems for Productions of Synthetic Hydrocarbon Defense Fuels (DOD Synfuels) from Air and Water, and was for 12 months of effort. Near the end of that time the CRADA was extended for one additional year to expire in August of 2006. The amended CRADA was NCRADA-NRL-04-350(1) and the SOW was modified under the NRL/GA joint tasks as described below.

The original CRADA included a set of NRL tasks including the development of methods to remove CO_2 from seawater, the selection of important fuel properties to strive for in the fuel production scheme, and the development of the chemistry to produce hydrocarbons from the CO_2 starting material (as opposed to CO starting material). Also, NRL was to select the best of any multiple options developed at the bench scale and assist GA in the plans to build a pilot scale system to demonstrate shipboard feasibility of the overall process.

The GA specific tasks included the selection of the best options to obtain CO_2 from air, the development of the best option to produce hydrogen, and the process engineering design for a pilot plant effort. The joint NRL/GA tasks included selection of the best option for CO_2, whether from air or seawater, development of the overall scientific and economic feasibility, evaluation of breadboard subsystems validation experiments, development of a systems concept design, holding one or more expert workshops to validate any concept designs, and to decide whether any process should be developed further, and if so, to develop a program roadmap.

The actual accomplishments of this CRADA during its two year life will be detailed in Sections 7.0 through 11.0 below, particularly the highly related effort that arose from the CRADA in developing the second DARPA proposal made in October 2004.

6.0   ESTABLISHMENT OF FIRST FUNDED NRL WORK UNIT TO SUPPORT SEA BASED FUEL SYNTHESIS IN FY05

We see that the NRL patent application was filed, and the CRADA on the Development of Systems for Production of Synthetic Hydrocarbon Defense Fuels (DOD Synfuels) from Air and Water was established shortly after April 2004. The final request of the NRL DOR in April 2004 was that a Work Unit be established with internal funding to support project work on Sea Based Fuel Synthesis. This WU was established as T009-05 with the Principle Investigator as Dennis Hardy beginning in October 2004 for $240K, or an approximate 10 man-month effort. This funding was to support the NRL portion of the NRL/GA CRADA specifically for carbon recovery from seawater and for initial work on carbon dioxide and hydrogen reactions at the bench scale using 1 to 10 grams of fixed catalyst beds.

This was actually the second NRL internally funded project, the literature search of March 2004 being the first funding. This WU, however, was the first to support actual experimental work in support of the patent application and the CRADA. The funds were also used in part in the development of the large industrial/academic consortium that began to form in August 2004 and culminated in a DARPA proposal in October 2004 described in the next section.

It should be noted that the original NRL/GA CRADA was to be funded internally by each participant at about the 1 person-year level for the first year. No funds were to flow in either direction. It was planned that DARPA or other outside funding would be sought as the project developed during the ensuing 24 months.

7.0   ESTABLISHMENT OF CONSORTIUM OF INDUSTRIAL AND ACADEMIC PARTNERS FOR THE SECOND DARPA PROPOSAL OF FY05

In the spring of 2004, Hardy gave a talk at a DOD Fuel meeting in NSWC Philadelphia where he summarized the NDU future fuels workshop of the previous year and mentioned the possibility of using environmental CO_2 from seawater as a shipboard source of carbon to make fuel in situ. One contractor present at the meeting was Charles Smith from Northrop Grumman Newport News (NGNN) and he was very excited about these ideas and began to encourage an NRL/NGNN meeting to discuss potential programs that might result from such collaboration. Smith was thinking of two potential long term projects. The first was the construction of a nuclear aircraft carrier specifically built not to store 5 million gallons of fuel, but to produce the daily required amount and store only a fraction of that amount. The second long term project would be to build a non-combatant nuclear vessel specifically geared to travel with a battle group and to make fuel for both aircraft and the battle group ships (i.e., NATO F-76 or what is actually commercial number 2 diesel fuel that meets Navy requirements for flash and storage stability). The modified CVN would produce about 100,000 gallons per day of jet fuel and the purpose built non-combatant would produce up to 500,000 gallons per day of both jet and diesel fuel.

The NRL DOR shared Smith's view regarding the future modified CVN as a potential long term naval goal and thus the stage was set to continue talks with NGNN personnel about future collaborations. Soon after the NRL CRADA was signed with GA and at the kickoff meeting in September 2004, the idea was discussed about forming a large consortium and offering a major proposal to DARPA that incorporated both the science issues that were being funded at a very low level internally at NRL and GA and also the further out technology and design issues that were as yet completely unfunded. Hardy and Dahlburg began assembling a team that included NGNN, Idaho National Energy and Engineering Laboratory (INEEL) (part of the Department of Energy (DOE)), INEEL managers BWX Technologies, Inc., General Atomics (GA), and the University of Maryland (UMd). In addition to this team which would make the actual proposal to DARPA, Hardy included participation from ONR and NAVSEA 05 surface ship requirements. NAVSEA 05 and GA were tasked to get endorsement from the Navy nuclear community, NAVSEA 08, but because the actual proposal was simply to initially use just typical CVN light water reactors, direct NAVSEA 08 participation in the proposal was not sought at this time.

In September 2004, just after the NRL/GA CRADA kickoff meeting, this larger consortium of approximately 22 contributors met at NRL for 2 days to outline a major DARPA proposal in response to DARPA Tactical Technology Office (TTO) Broad Agency Announcement (BAA)04-04 which was looking for alternative future energy schemes. The title, Sea-Based Fuel Synthesis for Logistic Independence, was chosen and assignments were made to the various organizations. NRL contributed to carbon capture from seawater and logistics fuel requirements, NGNN contributed to the overall project management and process integration modules, GA contributed to nuclear and hydrogen generation and carbon capture from air modules, BWX and INEEL contributed to technical management and fuel production, and UMd contributed to the carbon capture and fuel production modules. ONR and NAVSEA reviewed the contributions of the participants.

NGNN provided management of the proposal and made the actual presentation to DARPA TTO (Tactical Technology Office) in October 2004. The proposal was in 5 phases with the first phase being a rapid technology assessment over a 9 month period at an estimated cost of $500K (with an optional additional $130K computer modeling task), phase 2 being a technology selection, phase 3 being a system design, phase 4 being a pilot operation, and phase 5 being an implementation plan. The entire 5 phase project would take about 5 years and 9 months with a total estimated cost of $40 million. The final cost included the construction of a working pilot plant (land based) with a goal of about 1,000 gallons of hydrocarbon product per day.

The Phase 1 SOW tasks included the identification of sea based fuel production requirements such as fuel type, quantity, waste or byproduct handling, physical platform limitations, interface with the operational Navy, operational environment including marinization and combat issues. The carbon capture tasks included examining the basic physical and chemical processes to determine optimum process for CO_2 recovery using properly scaled bench scale experiments using actual and artificial seawater. Determine the rate limiting steps of CO_2 removal by practical physical methods. Determine the possibility of enhanced recovery rates by combining a variety of physical extraction processes, and provide an indication of potential selected methods for scale up and shipboard use. The other carbon capture task involved recovery from air by membrane gas adsorption, alternative absorbents and regeneration, materials constraints and system fabrication materials, and the space and weight limitations of this option. A third task was to determine the constraints on extracting carbon from turbine exhaust. The hydrogen production task was to compare 4 different technologies to determine the most feasible for scale up (electrolysis, high temperature electrolysis, 2 dimensional cell modeling, and thermochemical cycles). The hydrocarbon synthesis task was focused on optimization and marinization of existing gas to liquid schemes towards maximizing the desired hydrocarbon product, system size reduction, and most importantly assessing the technology dealing with direct conversion of CO_2 to hydrocarbon compared to a separate reverse water gas shift reaction. The conceptual configuration task involved establishing a near term (<10 years) integrated process that was as seamless as possible for shipboard systems. Also this task was to provide evaluation of longer term technology options (beyond 10 years). Finally a preliminary assessment of technological gaps would be made by the entire team and from that a research plan for phase 2 would be developed.

The overall program goal was to synthesize hydrocarbon fuels on board a naval vessel using nuclear energy. Initial calculations by the team showed that about 100,000 gallons per day would require about 320 MW(e) and would fit into a 350 m long ship providing jet fuel at about $2.50 to $3.00 per gallon. The goal was to provide a paradigm shift alternative to business as usual (BAU) and to vastly improve tactical operations and sea-basing. The actual fuel produced for aviation would ultimately be far superior to anything that could be refined from crude oil. The ability to make fuel near the fleet would greatly improved logistics since fuel represents the heaviest, largest re-supply to the Navy, exceeding food, spare parts and armaments.

The key technologies that require a science program include improved future hydrogen generation, carbon capture from water and/or air, fuel synthesis via new or improved gas to liquid schemes. This last technology has a large and on-going chemistry requirement. Of course, the entire scheme could be cobbled together using off the shelf (OTS) processes,

however, the overall process using existing technology would be extremely cumbersome and large and prohibitively expensive and energy inefficient. Thus, as an example of the first phase, the production of hydrogen would be expanded to include thermochemical cycles and higher temperature electrolysis concepts.

The potential dual use technology in the future is not immediately clear because there are no non-naval shipboard nuclear plants available. However, there are two long term changes that could make dual use very much more attractive and thus create a market that was almost 100 times larger than the DOD market for fuels. The first of these changes could be the development of small high temperature gas cooled (or gas turbine) nuclear reactors that could be made available for commercial purchase as a source of electricity either at sea or on land. The second change possible is the development of ocean thermal energy conversion (OTEC) on a very large scale of 100 to 200 MW. This second change would make the commercial production of hydrocarbons at sea possible without any need for nuclear electricity. Also, a combination of thermal and nuclear electricity production (at sea) could be envisioned depending on the commercial marketplace competition with fossil fuels.

There are US national benefits from this military prototype program and the science and technology needed to support it. First would be the reduction of national dependence on imported fuels. Second would be the reduction in net carbon dioxide emissions since the entire scheme from production through use would essentially be completely carbon neutral. This would also turn carbon dioxide from a pollutant to a national resource.

In March 2005, five months after this second major proposal to DARPA, the consortium was told by the reviewers that there was no interest in funding it. In discussing the DARPA decision there appeared to be a number of potential reasons, although really none of them had anything to do directly with the technical or funding parts of the proposal. First, the naval advisors to DARPA indicated that NGNN was remiss in not including specific endorsements in the proposal from NAVSEA 08 (the surface nuclear research office, in particular). Second, there did not appear to be any program managers at DARPA who could critically assess the proposal or compare it to other unusual alternative energy proposals. Finally, the proposal was deemed to be too applied and appeared to DARPA that it was just a series of cobbling together of existing systems rather than the need to do actual basic science and technology work in order to support the applied concepts of the project.

At that point most of the consortium members simply abandoned the project even though there had been intense interest and enthusiasm during the proposal writing. This left only the small internally funded NRL and GA CRADA agreement to keep the project alive. Actual experimental work from these CRADA partners began in about October 2004 and continued for the next two years and some of the as yet unpublished results of that period are described in Sections 8.0 through 11.0 below.

8.0   PHYSICAL EFFECTS OF TOTAL CARBON REMOVAL FROM SEAWATER

From October to December 2004 a series of simple experiments were undertaken to determine the magnitude and rate of total carbon dioxide removal from seawater when thin films were subjected to either vacuum (near or slightly above 20 $^{\circ}$C) or sparging with nitrogen near STP conditions. In addition the effects of slight temperature increase and the effect of time of the process were determined. The actual experiments were carried out primarily by Rachel Hodges, at that time a high school student volunteer at NRL.

We wanted these very simple feasibility experiments to be approximately in scale to full scale. This placed very difficult constraints upon the design of the simple laboratory scale experiments. At the planned full scale of about 400,000 L/day of fuel (about 380 metric tons/day) at least 10 billion L of seawater needed to be processed each 24 hour day. If we scale down about 100,000 times we need to process about 0.88 L of seawater per second in order to recover in the laboratory about 0.1 g of CO_2 per second.

At this time we had only a very limited supply of actual seawater from the NRL Corrosion Laboratory at Key West, FL, sampled in 1992 and stored in an airtight container. First, solutions of Key West (KW) seawater were spiked with known amounts of solid CO_2 by taking a 500 mL bottle with 250 mL of KW seawater and an air ullage of about 250 mL and adding the dry ice and capping the bottle until thermal equilibrium was achieved and then the pressure in the ullage was relieved. Finally, these solutions were allowed to stand for 2 days and the final spiked concentration of total dissolved inorganic carbon (DIC) was determined coulometrically [7]. Also a solution of $NaHCO_3$ was prepared in deionized water (DI) at a concentration similar to the total DIC concentration of KW seawater.

The experiments consisted of taking a standard aliquot of the solutions described above and measuring their total DIC content coulometrically before and after the process in order to determine the effect of each process on loss of total DIC as evolved CO_2 gas. The standard aliquot for these experiments was 60 mL. The first experiment was to pull 60 mL of water into a 60 mL syringe. This left an ullage in the syringe of about 5 to 7 mL of air. The syringe was inverted and connected via vacuum tubing to a water aspirator that pulled about 15 mm Hg vacuum (water temperature of the aspirator was about 20 $^{\circ}$C).

At the outset we would make up the spiked KW samples fresh and immediately test with the vacuum aspirator. There were two different amounts of additional CO_2 added to KW water, 150 mg/L and 300 mg/L. Recall that the KW originally contained about 100 to 120 mg/L of total carbon as CO_2. The samples had striking visual appearances from this simple test depending on the days allowed for equilibration before starting the vacuum test. Fresh samples would appear quite stable and quiescent until the vacuum was applied and then a rapid gas evolution of many small bubbles was given off and after 30 seconds slowed and stopped. When samples were allowed to stand 24 hours before vacuum testing a much lower number of very large gas bubbles would form on the syringe walls and slowly be de-gassed. When samples were allowed to stand 48 hours then only a very few tiny bubbles would appear on the walls during the vacuum aspirator testing.

The test times for vacuum aspiration were 30, 60, 120, or 240 second intervals. Not all data are reported in every test case since some test conditions produced very little change for all test times such as in Table 1. Finally, all samples after the vacuum or sparging or thin film testing were placed in 40 mL vials and sealed with no ullage in order to compensate for the time between the sample tests and the off line coulometric analysis.

Table 1. Change in CO_2 content (as total DIC) after 60 sec of 15 mm Hg Vacuum at about 20 ℃ using 60 mL Sample with 7 mL Ullage

Sample Description	Amount CO_2 Added (mg/L)	Time (sec) of Vacuum	Total DIC (µ mole/L water)	% CO_2 Change
Bicarbonate	100	0	2319	
		60	2353	-1
Key West	0	0	2021	
		60	1995	+1
Key West	150	0	3182	
		60	3172	0
Key West	300	0	4177	
		30	4204	+1
		60	4144	-1

Table 1 shows that simple vacuum treatment for relatively short times produces no change in either bicarbonate water solutions or in KW unspiked and CO_2 spiked samples. One would expect from the literature that the process of CO_2 equilibration from bicarbonate in solution would be a very slow one and take about 24 hours per L to complete since this is a diffusion controlled process. Diffusion of gas from liquid is probably not the slowest step in this process, however this will be discussed in detail later in Section 15.0 below. It is clear from the data that the crude method to increase the concentration of total DIC using dry ice was reasonably successful. One would think that in this system of seawater spiked with large fractions of gaseous CO_2 that this gas would be removed by the process. However, what is likely going on is that given the 24 hour delay between making the spiked samples and running the vacuum process experiment that the acidic dissolved gas was converted to carbonate and bicarbonate due to the buffering power of the bicarbonate ions already in the KW seawater samples.

Next we attempted to repeat the above experiment using one higher temperature of 40 ℃ to see if decreased CO_2 gas solubility would aid in the diffusion step from liquid to gas. In this experiment we used a 50 mL sample in a 125 mL Erlenmeyer flask. This flask was heated in a water bath to the desired sample temperature of 40 ℃ and then immediately exposed to the water aspirator vacuum for the desired length of time indicated in Table 2.

Table 2. Change in CO_2 content (as total DIC) after 60 seconds using 15 mm Hg vacuum at 40 ºC and 50 mL samples with an ullage of about 75 mL.

Sample Description	Amount CO_2 Added (mg/L)	Time (sec) of Vacuum	Total DIC (umole/L water)	% CO_2 Change
Bicarbonate	100	0	2303	
		60	2231	-3
Key West	0	0	2021	
		60	2017	0
Key West	150	0	3163	
		60	1967	-38

It is clear from Table 2 that temperature plays a major role in aiding the diffusion step and speeding up the removal of CO_2 from an actual seawater sample spiked with CO_2 gas. This is in spite of the fact that equilibration for 24 hours of the original spiked sample is probably occurring. However, as will be seen later, once the spiked amount (as CO_2 gas) was removed at a sufficiently long time or high temperature, the remaining total DIC was removed at the very slow literature value reported above. This has immense, and until now, not discussed, implications for anthropogenic CO_2 additions to the ocean. From these very simple laboratory experiments one may postulate that any additional CO_2 added to the sea from fossil fuel combustion is, in the short term, very likely to be re-equilibrated to the atmosphere as ocean temperatures rise, as they have been doing in the last 60 years. This idea will be elaborated upon in the concluding section of this report.

Next the effect of sparging 50 mL aliquots of these samples with nitrogen using a course glass frit was investigated. The sample was poured into a 125 mL Erlenmeyer flask and connected to a 4 L Erlenmeyer flask via a glass tube. The larger flask was then connected directly to the water aspirator vacuum source. When the vacuum was turned on the water from the smaller flask was drawn into the larger flask through the course glass frit (sparger). This allows the water to foam into the larger flask under vacuum and increase the surfaced area in a rapid manner. This experiment was only able to be conducted at one time (about several seconds) due to the nature of its set up. The results are in Table 3.

Table 3. Change in CO_2 content (as total DIC) after being drawn through a course glass frit sparger using 15 mm Hg vacuum at 20 ºC and 50 mL samples.

Sample Description	Amount CO_2 Added (mg/L)	Sparge?	Total DIC (umole/L water)	% CO_2 Change
Bicarbonate	100	No	2344	
		Yes	2190	-7
Key West	0	No	2021	
		Yes	1950	-4
Key West	150	No	3780	
		Yes	3006	-20

Again it can be seen that there was minimal effect with the bicarbonate and unspiked Key West seawater and a significant effect with the CO_2 spiked Key West seawater. However, again this effect is only operating on a fraction of the added gas only during these short experiments.

The above was then repeated by raising the temperature of the samples to 40 ºC before subjecting to the sparing. Again, the experiment was only run for a time that was dictated by the nature of the vacuum and the frit and lasted about one second. After that the water was recovered and stored in a 40 mL sealed vial with no ullage until the coulometric DIC content was determined. The results are below in Table 4.

Table 4. Change in CO_2 content (as total DIC) after being drawn through a course glass frit sparger using 15 mm Hg vacuum at 40 ºC and 50 mL samples.

Sample Description	Amount CO_2 Added (mg/L)	Sparge?	Total DIC (umole/L water)	% CO_2 Change
Bicarbonate	100	No	2303	
		Yes	2227	-3
Key West	0	No	2021	
		Yes	2002	-1
Key West	150	No	3206	
		Yes	1713	-47

Similar and predictable results can be seen when comparing the results of Tables 3 and 4. The only sample to lose significant CO_2 was the spiked Key West sample which essentially lost all of the added CO_2 and even part of the original bicarbonate content.

The final attempt at physically removing any significant fraction of the total DIC content of bicarbonate or seawater samples was the "thin film" experiment. In this experiment a standard rotary evaporator was connected to the water aspirator vacuum and a large 1000 mL round bottom flask contained a sample of 50 mL. The rotation was set at level 8 (several revolutions per second) and the vacuum applied for either one minute or 10 minutes. The resulting thin film was made in an effort to once again attempt to speed up the slow diffusion step of the process of re-equilibrating bicarbonate to carbonic acid to carbon dioxide. Since by now it was clear that the carbon dioxide spiked Key West samples were simply giving up the higher equilibrated concentrations we only used an unspiked Key West and a bicarbonate sample for this experiment. The results are below.

Table 5. Change in CO_2 content (as total DIC) at 20 ℃ using a thin film rotary evaporator at 15 mm Hg vacuum and a 50 mL sample in a 1000 mL flask.

Sample Description	Amount CO_2 Added (mg/L)	Time (sec) Thin Film	Total DIC (umole/L water)	% CO_2 Change
Key West	0	0	2010	
		60	1992	-1
		600	2123	-6
Bicarbonate	100	0	2509	
		60	2500	0
		600	2663	+6

These results are consistent with the sparging and bulk sample vacuum experiments above. Bicarbonate does not equilibrate at a sufficiently fast rate to be of use in a process at sea which would be very volume and time constrained. The increase in carbon dioxide content of the bicarbonate sample is simply due to the inherent imprecision of the coulometric method of total DIC content measurement. All results in Tables 1 through 5 are always the average of at least 3 coulometric determinations, however.

This work was completed by December of 2004 and this is the first open publication of the results. The main benefit of the experiments was the finding that the addition of the CO_2 into seawater would eventually (after 24 hours) equilibrate to the bicarbonate form. This was verified by measuring the pH of the seawater immediately after gas addition and after 24 hours. The driving force of vacuum removing the **added** equilibrated CO_2 would cause the seawater to become more basic and the additional bicarbonate would then disproportionate as a buffer into carbonate and carbonic acid and thus would quickly lower the total DIC content through ultimate removal of the carbonic acid decomposition into carbon dioxide and water. At the same time the seawater returned to its original pH and buffering capacity as before the carbon dioxide spiking. This is a crude approximation of what has been going on in the oceans for the last century by anthropogenic burning of fossil fuel. All of the carbon dioxide will end up in the ocean and may even equilibrate to bicarbonate. However, as the ocean warms (as will be discussed in Section 17.0 below), this experiment tends to confirm the fact that we should expect the added CO_2 from man to make its way back into the atmosphere and increase in partial pressure in accordance with Henry's Law.

9.0   INITIAL ATTEMPTS TO USE ANION EXCHANGE RESINS FOR TOTAL CARBON REMOVAL FROM SEAWATER

This work was completed at NRL from January 2005 through May 2005 and has not yet been incorporated in a written report until now. The results in Sections 8.0 and 9.0 were discussed as part of monthly CRADA meetings with General Atomics that will be discussed in Section 11.0 of this report. As with the simple physical experiments geared towards carbon removal, these initial chemical attempts to remove bicarbonate and recover the ion as carbon dioxide for use in a further chemical process were very simple scoping experiments. They are

based on the ability of anion exchange resins to exchange hydroxide with chloride, bicarbonate and sulfate in seawater in a static or flowing system.

Dorchak and co workers [8] used the commercial weak base anion exchange resin Amberlite IRA-67 which is a polyamine, with a moisture content of about 60% in a cyclical process to regenerate ammonium carbonate solutions. Ammonia was initially used as a stack gas scrubber and efficiently formed ammonium bicarbonate. The ammonium bicarbonate was sent to the anion exchange resin column as an aqueous solution and ammonium carbonate was recovered along with carbon dioxide during a regeneration step that used hot water. The ammonium carbonate was then used to further strip carbon dioxide from stack gases and subsequently regenerated from the resulting ammonium bicarbonate that formed during carbon dioxide sequestration.

Even though the molar solution concentrations of bicarbonate in seawater were much lower than those used by Dorchak, attempts were made to use the anion exchange resin to directly recover bicarbonate by seawater and subsequently regenerate the resin by contacting it with hot water thus releasing the carbon dioxide gas while regenerating the original hydroxide form of the resin in a cyclical process. The Amberlite IRA-67 used in our work was obtained in the base form from Sigma Co.

First an attempt was made to determine how much bicarbonate could be exchanged on a given weight of resin in a simple flowing system using seawater and to determine the effect of flow rate so that an estimate could be made of full scale requirements for resin in a shipboard environment at sea. The hot water regeneration of the resin was critical since no strong bases could be transported or used at sea in the amounts necessary to usually regenerate ion exchange resins during land based processes. 50 mL of as received wet resin was placed in 100 mL polypropylene syringes and held in the syringes by a plug of glass wool at the outlet end. The syringes could be clamped at both ends to prevent any drying from occurring before use. Six identical columns were prepared for these scoping experiments.

As a first step deionized water at 20 ºC was gravity fed through the resin beds and 50 mL aliquots were collected and analyzed for total DIC content and pH. Then 150 mL of Key West seawater was gravity fed through each resin filled syringe and collected at the outlet in 50 mL aliquots. This first set of experiments was geared to simply determine the maximum loading of seawater bicarbonate on the resin. Table 6 gives typical data for the deionized water wash that was used to wash each 50 mL Amberlite resin sample before subsequent seawater treatment.

Table 6. The effect of rinsing Amberlite IRA-67 resin (50 mL) with deionized water in 50 mL water aliquots on the total DIC content and pH of the effluent. DIC by coulometry using a 5 mL aliquot and pH by calibrated combination glass electrode.

Cumulative Aliquot Volume (mL)	Total DIC (μ mole/L)	pH of aliquot
Deionized water control	30	7.1
50	1,333	9.4
100	308	9.0
150	80	7.1
200	54	7.1
250	49	7.2
300	34	7.0
350	51	7.2
400	31	6.9
450	39	7.1
500	21	6.9

It is clear that the gravity fed flow of seawater over the weak base anion exchange resin used has allowed some of the bicarbonate anions to exchange onto the resin (displacing the hydroxide anion normally present). The first aliquot of deionized (DI) water has washed a significant amount of bicarbonate from the column (which is replaced by hydroxide ion from the DI water self ionization. This first aliquot is also just about the right pH for this concentration of bicarbonate. By the time 300 mL has passed over the resin the column is considered to be re equilibrated into the hydroxide form and ready for exposure to KW seawater.

Three resin columns were used to determine the amount of bicarbonate (total DIC) that was removed when known volume aliquots were gravity fed through the known volume of the anion exchange resin. Three aliquots of 50 mL of KW seawater were gravity fed through the vertical syringes used and each separate aliquot was collected at the resin exit. The effluent KW seawater was then subjected to total DIC analysis by coulometry and the loss of total DIC was assumed to have been exchanged onto the resin. When the KW seawater effluent total DIC value rose to the value of the influent KW seawater total DIC value, the experiment was stopped and the total amount of bicarbonate on the resin was calculated. The data for 3 of these experiments are shown in Table 7.

Table 7. The capacity of Amberlite IRA-67 anion exchange resin for bicarbonate from KW seawater. The total DIC by coulometry is in micromoles/L.

Column ID	Aliquot ID	Total DIC	DIC reduction	Total DIC Reduction
	KW Control	2010		
Column 1	0-50 mL	1508	503	
	51-100 mL	1873	137	
	101-150 mL	2010	0	640
Column 2	0-50 mL	1370	640	
	51-100 mL	1827	183	
	101-150 mL	1919	91	914
Column 3	0-50 mL	1188	822	
	51-100 mL	1736	274	
	101-150 mL	1827	183	1279

From the data it appears that the anion resin does remove significant amounts of bicarbonate from KW seawater and then quickly equilibrates during the third 50 mL aliquot of seawater is added. Clearly the nature of the experimental set up plays a part in the crude repeatability of the results in Table 7. Because of the difficulty of taking smaller aliquots and the difficulty in the sensitivity limits of the coulometric determination of total DIC, we were constrained to take rather large aliquots. Since the density of the resin is about the density of water then the total weight of the 50 mL is just over 50 grams. However, on a dry resin weight basis this could amount to just under 25 grams. Since it appears that on average the anion resin removes about 45% of the total DIC of KW seawater this would be about 2.7 mg $[CO_2]_T$ per 50 mL of resin, or about 5.4×10^{-5} g $[CO_2]_T$ per gram of wet resin. For comparison the KW control contains about 4 mg of $[CO_2]_T$ per 50 mL of seawater. Since a full scale (100,000 gal/day) process would require about 10,000 g of CO_2 per sec then this would require about 300 metric tons (MT) per second of process time. If the total process of capture and regeneration was only 10 seconds total then this would require about 3,000 MT of anionic resin. Although this is a very large weight and volume it is still within the constraints of an aircraft carrier size of ship.

Finally, we investigated the regeneration of the spent anion resins using a hot water process similar to the one proposed by Dorchak in his resin regeneration scheme. Dorchak would heat water to 80 ℃ and used nitrogen to bubble the hot water through the spent resin which released the adsorbed bicarbonate as carbon dioxide gas which he trapped in a solution of strong base. Given the nature of our experimental set up we could not use gas bubbling. Instead, we submerged our spent wet anion resin which still contained interstitial seawater in a water bath held at 80 ℃ for time periods of 15, 30 and 45 minutes. The syringes were closed at both ends and contained an air ullage of about 10 mL. At the end of the heat treatment times, 50 mL of deionized water was gravity fed through the column and collected in a beaker containing 50 mL of 0.5 M NaOH. The results are shown in Table 8.

Table 8. The effect of time on the efficiency of total DIC recovery as CO_2 after elution with 80 ºC water. CO_2 values in µmoles/L.

Sample ID	Total CO_2 on resin column	Dilution factor (x1.5)	Regeneration Time (min)	Regenerated CO_2 amount µmoles/L
KW 3	1279	1919	15	2650
KW1	639	959	30	2512
KW2	914	1371	45	2421

The dilution adjustment made in Table 8 arises due to the need to account for the respective total water volumes because the total DIC from 150 mL of KW used to saturate each resin bed is eluted after hot water treatment into a total volume of 100 mL. Thus the data from the second column of Table 8 (which comes from the data generated in Table 2) is multiplied by 1.5 to arrive at a value that would be expected if 100% of the CO_2 were recovered by the hot water regeneration. The fact that higher total DIC values are reached after the regeneration was originally attributed to experiment difficulties in excluding the absorption of carbon dioxide in the base trap. The other important tentative conclusion made from the regeneration experiment was that increasing the time of regeneration had no effect on the amount regenerated and in fact the regeneration time may be much shorter than 15 minutes.

Subsequent work on strong base anion exchange resins in both static batch work and dynamic flowing systems is the subject of a later publication (after the time frame of this report). That work found quite different results from the experiments reported herein. In that work the initial preparation of the anion resins was quite different, the actual bicarbonate capacity in seawater was found to be much higher, and the efficiency of hot water regeneration was found to be much lower. However, for the purposes of feasibility of anion exchange resins to remove DIC from seawater, the conclusions remain largely the same. This particular approach could be used dynamically on a large ship up to the full scale production range. The use of hot water to regenerate the resins which appears quite reasonable in this initial work was found later to be much more energy intensive and might actually be a reason to not select this process as the best for full scale carbon recovery.

10.0   INITIAL ATTEMPTS TO USE IRON AND SUPPORTED COBALT BASED CATALYSTS TO PRODUCE COMPLEX HYDROCARBONS (OIL) BY DIRECT CONVERSION OF CO_2 AND HYDROGEN USING LABORATORY SCALE REACTORS AND THE MECHANISTIC INSIGHTS FROM THAT WORK

The work described below was carried out between April 2005 and September 2005 by Nick Tran and Al Berry at NRL and represents the first attempts during this project to directly convert carbon dioxide and hydrogen to hydrocarbons and water. The major commercially developed processes start with reforming coal or natural gas through the use of steam or partial oxidation to produce the fixed stoichiometry of carbon monoxide and hydrogen which is fed into a catalytic reactor that employs pressures between 200 and 300 psi and temperatures between 200 and 300 ºC. The desired products from this catalytic reactor are typically higher hydrocarbons with an approximate equal volume of water formed as a side product. In this type

of reaction carbon dioxide is considered an unreactive or undesirable species whether it is a contaminant in the reactants or a side product from the water gas shift reaction that arises when the product water reacts with the reactant carbon monoxide in a competing reaction that produces hydrogen and carbon dioxide.

In a similar scheme to the one using carbon monoxide and hydrogen as reactants, there is the commercially developed Lurgi process which starts with carbon dioxide and hydrogen as the reactants that are fed into a copper oxide catalyst bed at similar temperatures and pressures. The conversion to methanol and water under these conditions is usually very high and since there is little or no carbon monoxide in the reactant stream, there is no participation of the water gas shift reaction in this process. It is a clean and direct synthesis of methanol. However, given the flash point of methanol this cannot be the process of choice on a shipboard based system. In addition, the energy density of methanol on a weight basis makes it unsuitable as a fuel for naval (or commercial) aircraft. It should be noted here that in the usual reaction between carbon monoxide and hydrogen the water gas shift is the reaction between the product water with reactant CO to form hydrogen (beneficial) and carbon dioxide (seen as unreactive or undesirable) products. The reverse of this reaction is called reverse water gas shift, the reaction between carbon dioxide and hydrogen, however this reaction results in water plus carbon monoxide because of the nature of the catalysts and/or conditions of the WGS process. In the Lurgi process it is the catalyst that results in the products water plus methanol instead of carbon monoxide and it is in the NRL experiments that the products are water plus hydrocarbons (plus oxygenated hydrocarbons). See Section 4.0 for additional details.

There has been work reported by Riedel and co-workers in Germany and by Davis and co-workers in the US on understanding the mechanisms and conditions necessary to convert carbon dioxide and hydrogen to higher hydrocarbons (C-6 to C-16 being useful goals) in the last 20 years. Their efforts tend to focus primarily on the great differences in substituting carbon dioxide for carbon monoxide rather than trying to force the reaction to the desired higher hydrocarbon products regardless of whether a supported or unsupported catalyst of iron or cobalt is being employed. Since the NRL envisioned process does **not** start with reforming of any fossil fuels but instead gets hydrogen electrically (from nuclear or thermal energy conversion) and carbon dioxide directly from seawater (or air), then we are not bound by fixed stoichiometries. This is an important variable that Riedel and Davis have not thoroughly investigated to date. In addition since we have access to the two reactants independently at all times, we are not constrained to processes that are simply fixed and employ recycle, but ones that can be very complex. We can construct zoned reactors with different temperatures, pressures, and various molar ratios of hydrogen and carbon dioxide to maximize reaction pathways and processes for higher hydrocarbon production. These variables are generally unavailable in typical gas to liquid processes which all start with reforming fossil fuels such as the Fischer Tropsch process that has been commercialized for the past 70 years.

Berry's experiments involved using a commercial iron catalyst (unsupported) available from SudChemie (Louisville, KY) in a continuously stirred thermal reactor at about 300 ºC and 200 psi total pressure. He used a vessel of 150 mL volume and charged it with 10 grams of catalyst which was reduced under hydrogen to the iron carbide form. In order to investigate the process as simply as possible, no inert oil was added to the vessel but the catalyst was stirred dry.

In the first experiment hydrogen and carbon monoxide in a ratio of 3:1 was employed. This was maintained for 6 hours and the experiment was repeated 3 times. The hydrocarbon products were analyzed at the end of the reaction time by gas phase IR and it was found that primarily methane with a very small amount of propane had been formed. It was not possible to obtain the conversion efficiency since the reactor was not equipped for hydrogen, CO or water analysis.

Next, Berry substituted carbon dioxide for CO and kept all other conditions identical including the dry, stirred catalyst of reduced iron at 10 grams. He repeated these 6 hour experiments 3 times, each time using a new catalyst sample that he reduced *in situ*. When the products of this simple reaction were analyzed he obtained essentially the same results as with carbon monoxide, a mixture of about 99% methane and 1% propane.

Given the relatively simple experimental set up using only the gas and solid phases it should be possible to hypothesize potential mechanisms for the two experiments which give similar products. In fact in the last 70 years, 3 different mechanisms for the CO plus hydrogen reaction have been devised, each one with mutually exclusive key intermediates [9]. The oldest of these mechanisms is known as the Fischer mechanism after one of the earliest German chemists to devise the catalytic conversion of syngas (CO plus H_2) to hydrocarbons plus water products. The chief intermediate in the Fischer mechanism is a carbide species formed by the reaction of CO with the catalyst surface (which we will denote as M~•, where M is a metal surface site with a potential bonding electron available on the surface denoted by ~•). In our notation this intermediate would be

$$M\sim\overset{\bullet}{C}H_2$$

Because the key intermediate to chain growth is a carbide species, this is also the alternate name for this mechanism. It is this key intermediate in the initiation steps that allows subsequent chain growth.

About 30 years later in the 1970's a second mechanism was proposed by Storch which largely replaced the Fischer mechanism. This mechanism was supported especially by Anderson and Kolbel and the key intermediate was the formation of an alcohol complex radical on the active metal surface site. Thus this mechanism was alternatively known as the alcoholic mechanism. In our simple notation this would be denoted as

$$M\sim\overset{\bullet}{C}HOH$$

After this initiation species was formed then chain growth followed.

Finally, several years later Pichler proposed a third possible mechanism for this simple gas-solid surface reaction where the key intermediate is a carbonyl type complex and the subsequent propagation and chain growth proceeds via the insertion of carbon monoxide to the growing chain. In our simple notation this intermediate would be

27

$$\overset{\bullet}{M\sim C}=O$$
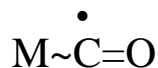
This mechanism is alternatively known as the carbonyl mechanism.

After 70 years, there is still no consensus on which of these mechanisms, each with a separate key intermediate species proposed, properly defines this very simple part of the free radical initiation step. Of course, the subsequent chain growth and termination steps are different depending on the initiation step. In Berry's very simple gas solid system where the catalyst is simply stirred rapidly in contact with the two gaseous reactants, we can postulate all of the following possibilities to form free radical intermediates:

M~ plus H_2 can react to form H~M~H, and each of the hydrogen atoms can dissociate from the metal surface to form 2 hydrogen atoms in the gas phase. Next, the diatomic hydrogen can heterolytically cleave to form M~H plus a hydrogen atomic radical in the gas phase. The M~H can subsequently dissociate to form a second hydrogen atomic radical in the gas phase. This is identical to the potential products of the molecular hydrogen first forming a complex on the metal surface before breaking the HH molecular bond and then forming 2 hydrogen atoms in the gas phase. Next, the carbon monoxide can break one of its bonds to form a complex on the metal surface in one of three possible ways. First the carbon can bond to the surface with the free radical on the oxygen atom. Second the carbon can bond to the surface with the free radical on the carbon atom. And finally, the carbon monoxide can bond to the metal surface through each atom leaving no free radicals on either atom.

In the first two cases of carbon monoxide bound to the metal surface, either bound radical can react with either diatomic hydrogen in the gas phase or atomic free radical hydrogen in the gas phase. For the case of the surface bound CO with the radical on the carbon atom this results in M~CH=O, which is Pichler's carbonyl key intermediate and in the case of the surface bound CO with the radical on the oxygen atom this results in

$$\overset{\bullet}{M\sim CHOH}$$

which is Storch's alcoholic key intermediate. The radical can further react with either gas phase diatomic hydrogen or gas phase atomic free radical hydrogen to form MCH_2OH which can further react with gas phase diatomic hydrogen or atomic free radical hydrogen to form water plus

$$\overset{\bullet}{M\sim CH_2}$$

which is Fischer's carbide key intermediate.

The same serial reactions are possible with the second of the two cases M~C=OH which results in the formation of M~CH$_2$OH and then water plus Fischer's carbide intermediate species. Indeed, there is a further set of reactions in the gas phase alone that can be postulated between carbon monoxide and atomic hydrogen atoms that would result in

$$\overset{\bullet}{C}H=O$$
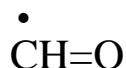
in the gas phase which would react with the M~ surface to form M~CH=O followed by reaction with H$_2$ or H$^.$ to form M~CH$_2$OH followed by reaction with gaseous H$_2$ or H$^.$ to form water plus Fischer's carbide key intermediate again.

In summary, we can see that in order to explain the gas-solid reaction of H$_2$ plus CO giving water plus methane, we must not ignore the importance of the gas phase reactions which are critical and key to explaining the overall mechanism. In general the 3 major mechanisms postulated over the last 70 years have done just that and ignored completely the gas phase reactions and their importance in the overall mechanism. The mechanisms by Fischer, Storch and Pichler pay undue attention to the liquid phase reactions on the surface and to the reaction steps between the gas and solid surface. By so doing they have each come up with a mutually exclusive overall mechanism that explains the initiation, chain growth and termination using 3 different, mutually exclusive key intermediates. By paying attention to the gas phase reactions as equally important (in our case we have no liquid phase reactions to consider due to the nature of our dry gas experimental set up) it turns out that all 3 key intermediates of the 3 different mechanisms arise in one generic mechanism to explain the production of methane (and eventually propane) from CO plus hydrogen.

When Berry substitutes carbon dioxide for carbon monoxide he forms essentially an identical product mix of methane with about 1% propane (plus water). Once a reasonable generic mechanism for the carbon monoxide reaction is known then it is not difficult to predict the products using carbon dioxide as a starting reactant. This is because the first step under his conditions is simply the reverse water gas shift reaction described above or reduction of carbon dioxide by hydrogen to form carbon monoxide plus water. The CO then simply reacts as mechanistically described above when it is just one of the starting materials. The importance of Berry's experimental finding is that one does not need a two step process involving two separate reactors, first the reduction of carbon dioxide (RWGS) and second the CO plus hydrogen reaction to hydrocarbons plus water; both reactions occur in a single reactor.

The above generic mechanism could also be used to predict the reaction of gaseous methanol plus hydrogen provided that the methanol could form

$$H_2\overset{\bullet}{C}OH \quad or \quad H_3C\overset{\bullet}{O}$$
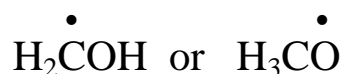
as an intermediate. In either case a reaction of this intermediate with the surface M~ would yield the necessary species to further react with either diatomic hydrogen or atomic free radical hydrogen to form water and the Fischer carbide intermediate. This intermediate is then able to further react with hydrogen to form methane and methyl radicals and then contribute to chain growth on M~ or to termination reactions leading to higher hydrocarbons. These experiments are yet to be tried.

One additional important point regarding a correct and inclusive generic mechanism for the reaction of CO or CO_2 on catalytic surfaces with hydrogen is made by C. K. Rofer-DePoorter in her classic review of 1981 *Untangling the water gas shift from Fischer-Tropsch: A Gordian knot?* This was later published as "Comprehensive Mechanisms for the Fischer-Tropsch Synthesis," Chem. Rev. 81:5, Jan. 1981. She states that it appears to be convenient to consider the water gas shift (and its reverse reaction) as a separate reaction to the chain growth reactions in some cases, but that a detailed examination of mechanisms indicates that WGS and syngas reactions **share several elementary reactions.** This means that reverse water gas shift cannot be separated either in a theoretical or practical way from syngas reactions and that the experiments to directly catalyze CO_2 and hydrogen to hydrocarbons are potentially viable means to the desired end without the need to separately and first reduce carbon dioxide to provide the syngas feed stock reactant. Indeed, future investigations to the ones described in this chapter should not overlook the possibility of mechanistic schemes that would produce diatomic oxygen as the major side product to carbon oxide reductions instead of water. The economic implications would amount to an incredible reduction in the need for expensive hydrogen reactant.

Tran's experiments differed in many significant respects from Berry's. First of all, Tran used a static fixed bed reactor which he maintained at the desired total pressure and stoichiometric ratio of reactants for up to 5 days. Tran used a standard synthetic process to make his catalyst (Gulf oil patent using cobalt and manganese doped with ruthenium on kieselguhr support) by the incipient wetness technique. He characterized this supported catalyst to ensure that the desired surface area and covering of cobalt, manganese and ruthenium had been achieved. He used one gram of catalyst placed at the end of a thick walled quartz tube that was about 2 cm OD and about 10 cm long, closed at the outlet end. The tube was placed in a s/s tube with a 2 cm ID and about 10 cm length with about 1 cm wall thickness. The s/s tube was connected to the gas mixer using high pressure s/s tubing and placed horizontally in a tube furnace and heated to about 220 ºC and the catalyst was reduced under hydrogen for 24 hours before charging with hydrogen and CO at a total pressure of 250 psi and a mole ratio of 3:1 hydrogen to CO. The pressure was checked hourly and maintained except during the night when the pressure was readjusted after about 8 hours.

At the end of 5 days the temperature was lowered and the pressure relieved and the catalyst bed was washed with methylene chloride to remove any organics that had formed. The methylene chloride was reduced in volume (from 10 mL to 0.5 mL) and the extract was analyzed by capillary column GC followed by quadrupole mass spectrometer detection. The capillary column was a standard 50 m SP2100 column which essentially separated complex hydrocarbons

on the basis of their boiling point. The temperature program was started at 100 ºC for 5 minutes and programmed at 2 ºC per minute up to 300 ºC. The injection volume was 1 µL split 10:1 onto the column. A complex total ion chromatogram was obtained with hydrocarbons detected between about C10 and C20 in a random carbon number pattern. The products included many which were oxygenated hydrocarbons (primarily ethers) and several which showed an indication of substituted aromatics (with and without oxygen incorporation in the substituents). This unusual product pattern is probably due to the nature of the experimental set up which would favor the highest chain lengths possible due to the very long reaction time and the static conditions of the intermediates formed. The formation of aromatics is unusual but can also be explained by the unusually long reaction times. As in Berry's work in the stirred reactor for shorter times, the analysis for water was not possible.

The next experiment that Tran performed was identical except that he substituted CO_2 for CO as the major reactant to reduce. After 5 days the catalyst bed was extracted and analyzed by identical GC/MS conditions. The complex total ion chromatogram obtained with CO_2 was quite different than that obtained with CO and contained fewer individual product species. However, it shared the CO product yield in terms of many oxygenated hydrocarbons formed, in the similar range of carbon number, and in the presence of several aromatic compounds being found. A definitive determination of most of the products was not possible by mass spectral analysis due to the complexity of the mass chromatograms and the lack of standards. However, the major conclusion from this work was that it was possible to directly reduce carbon dioxide with hydrogen using a cobalt/ruthenium supported catalyst at typical mild syngas experimental conditions and to produce hydrocarbon mixtures in the desired range of carbon number.

This represents the first publication of these initial oil making experiments at NRL. An invention disclosure was submitted and a patent application filed in 2006 for the cobalt based process of Tran. After this work was completed we became aware of a number of research laboratories and workers interested in this type of work. This includes work by E. Stechel at Sandia to use a solar process to reduce carbon dioxide and water to hydrocarbons and oxygen. Also a metal catalyst patent application of 2004 by Canadian R. Gagnon to convert carbon dioxide into hydrocarbons using hydrogen and nickel based catalysts. Also, similar work in Russia in 2005 to hydrogenate CO_2 over copper and nickel catalysts to produce hydrocarbons was reported [10]. Italian G. Centi reported attempts to use solar energy to reduce CO_2 to produce natural gas and methanol in 2006 [11]. Similar work by G. Olah, et al. at the Loker Hydrocarbon Research Institute at USC was reported in 2007 [12]. C. Kubiak et al. at UC San Diego also reported using solar energy to reduce carbon dioxide to fuel [13]. All of this very recently reported work along similar lines to our own at NRL indicates that this is indeed an area that many workers are investigating on an international basis.

**11.0   RESULTS FROM GENERAL ATOMICS (GA) UNDER THE NRL CRADA
AGREEMENT BETWEEN JULY 2004 AND AUGUST 2006**

Section 5.0 describes the history of the development of a CRADA between GA and NRL.
Sections 8.0, 9.0, and 10.0 describe the results obtained at NRL using the CRADA agreement as
the principle program guidance during the first year of the CRADA. Sections 13.0, 14.0, and
15.0 below will describe the NRL program during the second year of the CRADA. This chapter
will discuss in a general way the progress of GA during both years of the CRADA and also the
collaborative aspects of the CRADA. Finally, references will be given for the two major reports
that GA has already published after the end of the CRADA agreement.

The first joint meeting between the participants was at GA in San Diego in October 2004
and levels of effort were determined for the agreed upon tasks in the CRADA SOW. GA had
already been evaluating thermochemical production of hydrogen and had also begun its other
primary task of evaluating other existing means of hydrogen production and setting up an Aspen
Systems model for designing an overall process scheme. NRL had already begun its initial
studies into carbon dioxide recovery from seawater. No work on the joint tasks had yet been
done since most of the tasks required more information such as the selection of potentially
promising catalysts and processes for producing synthetic liquid hydrocarbons.

At the first joint meeting the main business was in assigning the tasks to the various
individuals at both facilities, detailing the actual task steps and generating a time line for the
entire 12 month period of the original CRADA agreement. A proposal by S. Lambrakos and J.
Michopolis of NRL to perform optimization modeling was made at this meeting but no action
was possible due to a lack of funding at NRL. Also GA presented their literature survey to date
on the feasibility of recovering sufficient carbon dioxide from the air on a shipboard platform.
The potential usefulness of membrane gas absorption (MGA) processes on a shipboard platform
were made by GA contractor L. Bogard.

By the time of the initial meeting at GA on the CRADA, the same GA and NRL
participants had already met at NRL in September 2004 as outlined in Section 7.0 above. The
status of the DARPA proposal was also discussed at the CRADA kick-off meeting, however, no
decision was to be made by DARPA until March of the following year and as indicated, it was a
decision not to fund the proposal.

Monthly meetings by video conferencing and teleconferencing took place during the
remainder of the first year. During the year GA visited a number of sites of industries involved
with carbon dioxide removal from air such as Kraverner in Houston, TX. GA also began to do
the economic analysis of constructing a shipboard platform with the information then at hand.
GA also visited Syntroleum Corp. in Tulsa, OK to observe their catalyst development laboratory.

In June 2005 the CRADA partners decided to amend the original agreement to extend it
for an additional 12 months to July 2006. At that time NRL revealed the development of the
new generic mechanism for gas to liquid reactions that was discussed in Section 10.0 of this
report in more detail. It was noted that the new mechanism predicted methanol and water would
result from the reaction of carbon dioxide on reduced iron catalysts unless the RWGS proceeds

32

faster in the gas phase than on the surface. If this occurred then the result would be minimal methanol production and the desired hydrocarbon production that was the result of A. Berry's experiments. Also at this meeting L. Bogart of GA discussed an improved fuel cost analysis incorporating elements of the overall process and also discussed the Mobil methanol to gasoline process and how it might relate to the future of the project.

As Navy interest continued in the project at only a very low level, GA decided after the second 12 month period of the CRADA to withdraw from further collaboration. At the conclusion of the CRADA GA issued two separate reports that formally documented the entire two years of participation and results [14, 15]. Several major conclusions can be summarized. First, thermochemical production of hydrogen remains one of the best and most efficient and least costly options. However, there are two roadblocks to this technology: (1) the high temperatures required are not available on light water reactor ships; and (2) scaled up reactors to produce the required 150 metric tons per day of hydrogen have not yet been built. The first roadblock could be overcome by the Navy's selection of a high temperature gas cooled reactor. A second major conclusion was that technologies do exist to economically remove carbon dioxide from air in sufficient rates for a full scale production of fuel. However, the actual MGA itself would take up a very large volume for a shipboard application and it would be very difficult to design into existing platforms.

12.0   FUNDING AND PLANS FOR FY06

As indicated in Section 4.0, Code 1001 provided $35K towards this project for a literature survey in FY04 and the equivalent of approximately $250K allocated by a job order number in FY05 to support NRL efforts in the CRADA with GA. No other funding from ONR or DARPA was able to be identified for the project. Given the progress to date as of September 2005 and the continuing interest in the project by GA through most of FY06, Code 6000 (B. Rath) actively sought internal funding through Code 6100 to continue the project tasks within NRL through FY06. An amount approximately equivalent to $250K was identified and Hardy agreed to submit a basic science (6.1) proposal in October 2005 to the NRL RAC which if funded in the competitive process would begin a 3 year program in FY07 with possibly one to two years extension beyond that given the success of the project tasks. That would continue a funding line out to FY09 and possibly FY11. The details of that proposal and the associated funding problems will be given in Section 16.0.

The FY06 funds that were identified for this project carried with them specific goals. First, N. Tran was to design, build and test a high pressure membrane extractor to attempt to determine the permeation rates of carbon dioxide from seawater with the assistance of D. Hardy. The results of this work will be described in Sections 13.0 and 15.0 below.

In addition Tran was to scale up the original experiments that he had completed in the fixed bed reactor using kieselguhr supported cobalt, manganese, and ruthenium catalyst the previous year to a much larger scale. In the original experiments about 2 grams of catalyst had been used and the plan was to build a larger continuously stirred thermal reactor system and use 10 to 50 grams of catalyst for each run. The scale up was to be the major part of this task, but if

all went well with scaling, then additional parameters were to be more carefully examined including varying the hydrogen-carbon ratio during the reaction and varying other parameters such as pressure and temperature. The product analysis was to be done by both Tran and Hardy. This work was eventually not completed in FY06 but was done under ONR contract to the University of Kentucky during FY07 and at NRL in FY08/09 and is reported in separate publications.

Finally, for FY06 Hardy was to continue to try to improve the ion exchange recovery of bicarbonate from seawater using the weakly basic anionic exchange resins and to extend this work to strong base resins and then to acidic cationic resins. He would be assisted in this work by a number of college students including R. Hodges and C. Williams. The results are discussed in Section 14.0.

At this point it should be noted that Hardy non-voluntarily retired from full time federal service in June 2006 but to enable his continued contributions to the project at this critical time he agreed to be re-employed as a part time intermittent federal annuitant and the paperwork was completed and approved by the Secretary of the Navy so that he could return to work in September 2006 and this appointment was able to be continued for the next 4 years.

13.0   INITIAL RESULTS OF THE HIGH PRESSURE (1,500 PSI) MEMBRANE EXTRACTION OF CO_2 FROM SEAWATER

In the fall of 2005, Tran and Hardy constructed a laboratory scaled CO_2 extractor from seawater under 1,500 psi pressure using as the central feature multiple layers of a commercial hydrophobic gas permeable membrane from Celgard made of polypropylene. The membrane chosen was Celgard 2400 with 37% porosity, 0.117 x 0.042 micron pore size (note the pores are rectangular in shape), 25 micron thickness, 1300 kg/cm^2 tensile strength which was cut to fit in the specially fabricated membrane holders which were essentially based on Swagelok high pressure 316 s/s unions. The Swagelok unions mandated a circular membrane geometry of 0.618 cm diameter. The membrane multi layers were supported on a s/s sieve support/frit of 0.618 cm diameter and thickness of 1.0 mm with an effective pore size of 0.5 microns.

Two complete extractors were built for these initial scoping experiments. Each one consisted of two identical 316 stainless steel cylinders with a volume of 500 mL and a 0.28 cm wall thickness with 4.42 cm inner diameter and about 29 cm length. The cylinders were mounted vertically and the top cylinder was connected by 316 s/s tubing to an ISCO LC-5000 syringe pump which was used to charge the top cylinder with Key West Seawater and to obtain the pressure needed at the beginning and during the entire extraction period. Valve 1 is a high pressure shut off valve (all are of s/s interior construction) used to isolate the pump from the top cylinder. Valve 2 is located at the bottom outlet of the top cylinder and is connected to the membrane holder. Valve 3 is located at the outlet of the membrane holder and the top of the second cylinder whose original design function was to trap any gases passed by the membrane for later analysis. Valve 4 is located at the bottom outlet of the bottom cylinder.

The heart of the extractor is the Swagelok union holding the membrane. This is made leak free not in the normal fashion but by forming the Swagelok ferrule to tube connection slightly offset so as to precisely accommodate the depth of the s/s frit, the multiple layer membranes themselves, and a thin, flat Teflon washer whose purpose is to form the top seal of the polypropylene membranes.

The operation of the extractor is to open valve 1 and close valves 2 through 4. The ISCO pump then charges the top 500 mL cylinder with seawater and pressurizes the top cylinder to 1,500 psi (100 atm), or any other lower pressure desired. After leak checking for 5 minutes at pressure, valve 1 may be closed and only opened during the time of the experiment to monitor the total pressure of the entire system. At time = 0, valves 2 and 3 are opened but valve 4 remained closed. The bottom cylinder is thus originally at about 15 psi (1 atm) of air. The first experiment was with 4 layers of membranes for 2 hours and 58 minutes. The second experiment (using a second complete extraction apparatus) was for 23 hours and 50 minutes and used 12 layers of membranes. The third experiment using a fresh aliquot of seawater was for 80 minutes using 18 layers and the fourth experiment was using 14 layers for 80 minutes. At the end of the arbitrary extraction times chosen, valve 1 was shut and valve 4 was opened and then the top cylinder pressure was allowed to depressurize by retracting the ISCO syringe pump piston.

Aliquots from all 4 experiments above plus companion samples aliquots taken before the pressurized extraction times were analyzed about one month later for total dissolved inorganic carbon (DIC) analysis by standard coulometry procedure. The aliquots were stored at room temperature in a gas tight bottle with no gas ullage above the liquid. In the first experiment when valve 4 was opened a mixture of pressurized gas and some liquid was noted. This means that either some water permeated through the membranes or, more likely, around the edges of the membranes due to the very difficult nature of making the top seal. The amount of water was less than 1 mL. The remaining 3 experiments also gave evidence of pressurized gas buildup in the lower cylinder during the extraction, but gave no evidence of any water permeation. Because we did not have access to a CO_2 gas analyzer, the planned gas analysis from the bottom cylinder was not carried out. The results for the loss of total DIC from seawater from CO_2 gas permeation was measured as the difference in total DIC in the before and after aliquots. The results of this loss of total DIC are given in Table 9.

Table 9. Percent reduction of total DIC due to loss of CO_2 through the membrane.

Experiment and Conditions	% reduction in Total DIC/CO_2
1 – 4 layers 2 hours 58 minutes	92
2 – 12 layers 23 hours 50 minutes	92.5
3 – 18 layers 1 hour 20 minutes	33.9
4 – 14 layers 1 hour 20 minutes	75.5

Given the nature of the experimental conditions and the membranes involved and the nature of their operation, the results of these first 4 experiments indicated an incredible degree of success. When the aliquots from the post extraction experiments were measured for pH they were all between pH 3 and 4. At the time, these pH measurements seemed to be too low and later work proved that indeed they were too low. If the efficiency of removal of total DIC/CO_2 that was measured was real (and it most likely is) for these experiments one would indeed expect

the pH of the post extraction aliquots to be lowered from the original 7.8 pH of the Key West seawater employed. However, the pH could not drop below about 7, even with 100% reduction in total DIC.

The ultimate explanation deduced about 8 months later for the low pH measured was that the original top cylinders containing seawater had not been cleaned thoroughly enough and must have contained some acidic species that desorbed from the walls during the experiments and contaminated the seawater causing the pH to shift very low. It was this pH shift that caused the incredibly efficient reductions of total DIC/CO_2 in these 4 experiments and not simply the action of degassing through the gas permeable membrane layers. Unfortunately this was not discovered until after January 2006 when an invention disclosure had been filed (Navy case number 98,075 "High Pressure Extraction of CO_2 from Seawater") after many attempts to repeat the original experiments.

Originally the s/s cylinders containing the seawater for the extraction experiments were all cleaned with tri solvent (1:1:1 of toluene, acetone and methanol) to remove polar materials and this was followed by water washing followed by hexane washing to remove any possible organic material. Whatever the nature of the acidic absorbed species, it was efficiently removed by the basic seawater and so removed. Thus in any subsequent experiments the acidic contaminant had finally been removed from the walls and the seawater simply remained a constant pH of 7.8 during the time of the experiment. The actual measured rate of CO_2 extraction under the conditions of our work was 3.18×10^{-5} g/cm^2-sec. This would be considered a reasonable rate and so the invention disclosure was filed without realizing the real nature of the dramatic reduction results. Using our original extraction rate allows us to calculate the actual expected reduction rates under these experimental conditions of about 10%. This will be discussed in Part 15 below in more detail. In addition the work described in Section 15.0 and much subsequent work has now been published in several NRL reports and in a number of refereed journal articles.

14.0   RESULTS OF STRONG ACID CATION EXCHANGE RESIN WORK ON RECOVERY OF CO_2 FROM SEAWATER

This part of the project was completed from October 2005 through May 2006. It involved examining the use of strong acid cationic exchange resin beds in laboratory scale flowing systems. These sulfonic acid modified resins were first challenged by flowing seawater through the resin bed. As the sodium, potassium and other cations exchanged with the resin protons, the seawater would become quite acidic and depending upon the actual conditions and relative amounts of resin to seawater, the effluent could achieve extremely low acidity down to pH 1.0. Once the resin bed was exhausted, the first method of choice was to try to regenerate it using de-ionized (DI) water rather than the normally used aqueous acids. This is because of the necessity to regenerate at sea where large volumes of acids are neither available nor safe to handle. Surprisingly this regeneration was possible provided that extremely large volumes of DI water were used, regardless of the regeneration time.

It was found that the cationic exchange resins could liberate the equivalent of 30 mg of CO_2 per g of resin and that when the effluent seawater was acidified to about pH 6, greater than 90% recover from a given volume of seawater was possible. This is because once the seawater reaches this acidity the bicarbonate (and carbonate) species are converted to undissociated carbonic acid which then extracts very quickly as it breaks down to gaseous CO_2 and water, (>2,000 µ mole/L-sec). The problem is that DI water regeneration requires almost 5,000 gallons of fresh water to regenerate enough resin to produce enough carbon to synthesize one gallon of hydrocarbon fuel. The actual details of this part of the report can be found in NRL Memorandum Report 9044 [16].

15.0 RESULTS OF GAS PERMEABLE MEMBRANE EXPERIMENTS TO RECOVER CO_2 FROM SEAWATER AT PRESSURES BETWEEN 1,000 AND 450 PSI.

This work was completed by E. Ndubizu and D. Hardy in the summer of 2006 and involved the construction of a new apparatus without any wall contamination effects that plagued the Section 13.0 results reported above. Some of the improvements included the use of new monel high pressure liquid reservoirs, the ability to stir the pressurized seawater, the use of both ¼" and ½" unions to hold the membrane layers, and immediate sample analysis after the actual pressurization time. In general these more carefully run experiments allowed us to determine the actual rates of CO_2 removal as a function of pressure of the bulk liquid, in addition to membrane surface area. These experimental details and results are also now available in NRL Memorandum Report 9129 and refereed publications [17,18,19].

In general this work verified that the complex bicarbonate system in seawater was capable of being manipulated by the experimental setup so that up to 10% of the total DIC per unit volume of seawater could be recovered from this static closed system. Membranes have long been used at or near atmospheric pressures of water to degas the 2% of CO_2 (v/v) that is typically available from seawater in open systems using large flow rates and typical commercially available polypropylene based gas permeable membranes such as the ones employed in our work to date. Unfortunately, the experimental permeation rates that we obtained for our special laboratory scale "closed system" experiments at pressures between 450 and 1,000 psi were much lower than those obtained at atmospheric pressure in open systems. Thus, the result that we can actually obtain 5 times the volume of gas as in the atmospheric pressure case still need to be addressed by experiments using the much more difficult open system at higher pressures.

16.0 PROPOSAL TO NRL MANAGEMENT FOR INTERNAL FUNDING FOR A BASIC SCIENCE EFFORT FOR 3 TO 5 YEARS BEGINNING IN FY07 (OCTOBER 2006).

As indicated in Section 12.0 above, the funding for this project in FY06 carried with it the requirement that the PI (D. Hardy) would openly compete for future project funds by making a formal proposal to management based on the basic science issues that needed further addressing as of FY07 through FY09. Provided this embryonic proposal made sufficient

progress, there was the option by the Chemistry Division to extend at some level the funding and program to FY10 and FY11. The proposal was briefed in October 2005 (FY06) to the NRL Research Advisory Council and was ranked as number 2 out of the ~ 160 proposals presented. Unfortunately, the funding requirement details were not coordinated between the PI, the Chemistry Division, and the upper management at NRL and this resulted in a minimally funded effort of only about one person year per year. The tasks as proposed required about 1.4 full time equivalent person years per year plus 2 full time post doctoral person years per year.

The proposal focused on the basic science issues in the two major areas of the overall project since its inception at NRL: (1) carbon recovery from seawater and (2) CO_2 conversion to fuel hydrocarbons. These areas are subject to all of the other many future shipboard constraints such as space and weight, in addition to the constraints of cost and even of engineering feasibility. However, the particular proposal covered only basic science issues to be addressed in 3 to 5 years and how these basic issues impacted on the next and very closely related step of transitioning to the applied science arena. In fact, it was almost impossible to brief the proposal without constantly referring to the exploratory and applied science issues. At one point late in the briefing several RAC members were exasperated enough by the delay in coming to the basic science questions to demand that this be addressed immediately.

In fact this basic science oriented proposal was titled, "Sea-Based Fuel Synthesis for Future Naval Applications". The actual specific science issues to be addressed included investigating alternative, more complex chemistry systems for potential regeneration of both cationic and anionic resins to recover seawater carbon; electrochemical regeneration schemes for both cationic and anionic resin regeneration schemes; open system membrane permeation rates using higher pressures and potentially modified membrane surfaces to increase these rates; determination of equilibrium values of ions in seawater with various resins; determining kinetic rates of exchange with seawater ions and the various resins using the complex mixtures available; and attempting to determine scaling factors for the laboratory scale experiments for all of the above. Because even these modest tasks were beyond the even more modest funding said to be available for this high priority project, none of the potential basic science issues involved with the complex free radical gas-solid phase chemistry of carbon conversion to higher hydrocarbons could be included in this NRL internally funded effort when it finally commenced.

Although the mandated funding that was offered at the time of the proposal grant was only $100K, this was later amended by the NRL management to approximately $250K per year and so at least maintained the level of internal funding from FY05 and FY06. The subject of the so-called "third" DARPA proposal for external funding for this project is covered in the final Section 17.0 below.

17.0   STATUS OF THE PROJECT AS OF OCTOBER 2006 (BEGINNING OF FY07) AND FUTURE PLANS.

From a personnel point of view, as of October 2006 there was only one full time federal scientist at work on the project, primarily because of the lack of sufficient funding to accelerate any of the many needed areas. This lack of funding may have been partially tied to the fact that

the PI retired in June 2006 and was only available one quarter of a man year after that. In addition, the remaining federal scientist decided to leave NRL (by May 2007). These problems conspired to minimize the amount of publication of results despite the fact that most of the findings supported continued efforts to increasingly approach technology areas which would further accelerate the ultimate project goals. This was offset by the assignment of Dr. Heather Willauer as the new PI for the project beginning in October 2006, at half time and then after May 2007 at full time. She was able to begin the publication of all of the work since the summer of 2006 as NRL memo reports or in refereed journals. It should also be mentioned that this project has been conducted as part of Dr. Fred Williams' Navy Technology Center for Safety and Survivability (NRL Code 6180) since its inception and has benefited from his management support continually.

Clearly, during the first five years of internally funded NRL effort, every road block led on to another avenue of investigation that always pointed forward. This is particularly true of the carbon capture area where it became apparent that physical effects would never meet the immense amounts of carbon rates required ultimately. As carbon recovery efforts have turned to more complex and more chemical efforts, some of these efforts, even when successful in the laboratory, do not stand up to the full scale requirements (such as cation exchange regeneration). However, even in this case, the results lead forward to even more exciting ideas such as electrochemical regeneration.

The carbon conversion area is really still in its infancy with many possible future directions to examine (in October 2006). Even the very rudimentary results to that date indicate the exciting possibilities of improving the free radical chain branching schemes far beyond those investigated in the last 80 years.

In the fall of 2006 NRL Code 6000 was successful in soliciting interest at DARPA to submit a proposal to the Innovative Tactical Technologies Office (Dr. E. Van Reuth) in response to their BAA 07-20. This proposal entitled "Sea-Based Synthetic Hydrocarbon Fuel for Enhanced Operational Readiness and Logistics Independence" was submitted by Northrop Grumman Newport News as the industrial lead and NRL listed as the support laboratory for the effort. This was identified by DARPA as a "seedling" project with potential funding at about $500K per year for up to 3 years, depending upon continued success at the end of each year's effort. This was an attempt by Willauer and Hardy to obtain the necessary total funding package to accelerate the carbon capture work partially funded by internal NRL funds and to accomplish additional work in the carbon conversion to oil area and to begin to accomplish some of the necessary applied work (to be completed by NGNN) such as the estimates for space and weight allowances for shipboard fuel synthesis systems. This latter task was to specifically determine if trade-offs were possible aboard any of the currently operating CVNs to accommodate the various potential full scale technology choices or even any potential smaller scale or pilot plant operations. This "third" proposal was presented to DARPA in June 2007. During the next 12 months and after much discussion and negotiation, a decision was made not to fund this proposal. The continued precarious state of funding for this project led by NRL efforts for its first 5 years will be the subject of future reports.

**17.1   Status Of Questions Regarding The Effect Of The Overall Project On Current
        Environmental Concerns**

Except for indicating in proposals and papers written after October 2006 that the overall
process appears to be carbon neutral, no attempt has been made to actually answer some of the
original questions raised by T. Coffey in private communications to D. Hardy as early as 2002.
Coffey's questions hinged on understanding the cyclical nature of a process that would take
carbon dioxide out the ocean (in large part as the bicarbonate ion), chemically incorporate this
into a liquid hydrocarbon and then ultimately burn it to recover the stored energy, carbon dioxide
and water. At what rate is the entire carbon cycle completed? Clearly we can determine the loss
of bicarbonate from the ocean by this process, but at what rate does the atmospheric CO_2 return
to the ocean and re-equilibrate as bicarbonate to actually complete the claimed carbon neutral
cycle.

These questions have not been addressed in part because there have simply been more
important questions to answer during the early stages of this project and in part because of the
lack of any funding to date to do more than keep abreast with the copious literature regarding the
effect of anthropogenic fossil fuel emissions on the global environmental scale. In a way this has
allowed people associated with this project on a part time basis the luxury of looking at the
effects of fossil fuel emissions from a completely fresh viewpoint. This section of the report will
outline some of this unique thinking and its implications on answering Coffey's questions.

If one first calculates the heat energy content increase of the top 300 meters of ocean and
the bottom 8 km of atmosphere (essentially the troposphere), based upon the temperature
increase in the last 50 years of each system (ocean increases about 0.3 °C and atmosphere about
0.7 °C), the weight of each of these systems and the respective heat capacity of air and water, one
finds that the heat energy increase of the ocean is over 50 times greater than the atmosphere. In
fact if the top 1,000 meters of ocean are included, the ocean heat energy increase is about 170
times greater than the atmosphere. This number can be calculated easily and can also be seen on
NOAA web sites (the ocean number is on the NOAA ocean website and the atmosphere number,
both in exojoules, is on the NOAA atmosphere website home pages as they existed in 2007).
Obviously, these two NOAA sites from 2007 did not communicate with each other. Since global
warming must be the sum of the warming in the two systems and essentially all of the warming
(heat energy increase) is in the ocean, then it is irrelevant to even discuss a physical effect like
the "green house gas" effect in the atmosphere. Indeed, it becomes absolutely necessary to
determine just what is causing the overwhelmingly important ocean warming. The heat energy
increase of the troposphere is about 3,460 exojoules and of the top 300 meters of ocean about
154,463 exojoules for the past 60 years.

Certainly, the anthropogenic burning of fossil fuels in the last 50 to 60 years is the root
cause of this immense heat energy increase. This means that carbon dioxide and other important
oxides like sulfur and nitrogen oxides are the chemical basis of ocean warming. If one postulates
that all three of these acid gases from anthropogenic fossil fuel combustion has a very short
lifetime in the atmosphere and the ultimate sink for most of the acid gases is the ocean, then the
enthalpy of mixing of these gases in water can be used to test out this postulate.

However, one has to explain 3 things in regard to overall total global warming in the last 50 to 60 years and all 3 must be tied to anthropogenic sources. First, what is causing the warming of the ocean; second, what is causing the pH drop of the ocean, and third and least important; what is causing the warming of the atmosphere. Since the anthropogenic SO_X emissions are known globally very precisely for the last 60 years we can calculate a drop in pH of the ocean upper, well mixed layer (defined as the top 100 m) caused by SO_X alone. We know the volume of this depth of water and its pH and we know the total amount of rainfall per year and will postulate that all of the SO_X is removed to the ocean within days of its entry into the lower troposphere. When we do this calculation we find that SO_X alone should account for a pH drop of about 0.15 pH units in the upper ocean layer in the last 60 years. This is almost exactly what Levitus and ONR have found from global sampling over the last 60 years.

When we calculate the contribution of CO_2 to the drop in pH in the ocean we find that since carbonic acid is a weak acid, as the concentration increases in the ocean that the first ionization reaction is forced to the left, and so anthropogenic CO_2 contributes only a very small fraction of the pH drop that has actually been measured in the last 60 years. This is in spite of the fact that the actual weight of CO_2 is almost 100 times greater than the weight of anthropogenic SO_X. The reasons for the inordinate effect of SO_X and NO_X is that they are both 1,000 times stronger acids than carbonic acid. Below we will deal with the important assumption being made here that all of the anthropogenic CO_2 enters the ocean after a very short life in the atmosphere (days to months at most).

Since we know the enthalphy of mixing of SO_X and CO_2, we can calculate the total amount of heat energy that each of these acid gases contributes when mixed into the top 300 m of ocean depth. We find that the sum of these two heat energies equals the actual measured temperature rise of the ocean over the last 50 to 60 years as measured globally (about 0.3 °C). In fact, the contribution of all of the anthropogenic CO_2 is about 80% of the total heat energy and the contribution of anthropogenic SO_X is about 20%. This verifies our original assumption that the enthalpy of mixing of these two acid gases is the entire cause of anthropogenic ocean warming. More importantly, it provides the evidence that the lifetime of all of the CO_2 from fossil fuel burning is very short (days to months).

But if all of the anthropogenic CO_2 and SO_X are dissolving in the ocean over the last 50 to 60 years, then why has the CO_2 concentration in the atmosphere risen steadily over that time frame, as has the carefully measured temperature of the atmosphere? One of the participants in the carbon capture work at NRL, Naval Reservist CAPT Kathy Lewis, helped uncover the answer to this question in the book "Carbon in the Geobiosphere" by Mackenzie and Lerman [20]. This very carefully written book allows one to calculate the contribution of the ocean bound CO_2 to the atmosphere as a function of ocean warming over the last 50 to 60 years. Over that time frame the warming of the ocean by the chemical mixing of the weak and strong acid gases described above has simply lowered the CO_2 solubility in seawater. The solubility of CO_2 as a function of seawater temperature is 3.746×10^{-2} at 15 °C and is 2.839×10^{-2} at 25 °C. This allows us to calculate the temperature dependence (which is nearly linear over this small range) as 0.00907×10^{-2} per 0.1 °C. Since we know that the measured temperature rise of the top 500 m of ocean is about 0.3 °C (this, of course, includes the top 100 m of well mixed layer in addition to the additional 400 m layer below this layer) then the decrease in CO_2 solubility in the ocean over

the last 50 to 60 years has been about 0.02721×10^{-2} decrease. This amounts to a decrease in CO_2 solubility over this time frame of about 0.726%.

We have postulated that all of the anthropogenic gaseous CO_2 rapidly dissolves in the ocean. There it is in equilibrium with the overwhelmingly larger bicarbonate buffer system. Do the actual kinetics of bicarbonate and carbonate conversion to CO_2 and the ionic diffusion rates of this system support a calculation of the potential loss of CO_2 from the ocean to the atmosphere? The kinetics of bicarbonate conversion are very slow. According to Stumm and Morgan it takes about 24 hours for the entire conversion of bicarbonate to CO_2 per liter of seawater provided there is a removal mechanism for CO_2. In our case the removal mechanism will be simply the decrease in solubility with the average temperature increase of the ocean over a 60 year time frame.

Next, we need to calculate the ion diffusion rate. For bicarbonate and essentially all the monovalent ions in seawater the ion diffusion rate, D, is very slow and about 10^{-5} cm^2 per second. This means that over large distances, such as the bottom of the ocean to the top (about 5 km) it would take about 25×10^{15} seconds for bicarbonate or most other ions to diffuse. However, over very short distances, e.g. 1 micron, the diffusion rate is much faster, about 1 millisecond. Over micron distances the rate can be calculated as 10^{-4} $cm/10^{-3}$ second or about 0.1 cm/second. Since the concentration of the entire bicarbonate system is essentially invariant from the surface to the bottom of the ocean, then we can estimate that within 50 to 100 days the re-equilibration due to loss of CO_2 from the ocean to the atmosphere of just the top layer would reach even to the bottom of the ocean.

Thus, for both time constraints, kinetics of gaseous CO_2 removal and kinetics of bicarbonate ion diffusion, the process can be thought of as happening in a matter of months to reach equilibrium. If the so-called pre industrial (before 1900) concentration of CO_2 in the atmosphere is taken to be about 280 ppmv (page 9 in the Mackenzie book) this amounts to about 6×10^{17} g of carbon. The total dissolved inorganic carbonate reservoir of the ocean is about 3.74×10^{19} g carbon. First we will calculate the amount of carbon lost from decreased solubility in just the top 100 m of ocean. This top 100 m contains about 7.48×10^{17} g of carbon and 0.726% of this would be about 0.054×10^{17} g of carbon lost from the ocean to the atmosphere as a function of ocean warming over 50 to 60 years. In order to reach the current levels of measured CO_2 in the atmosphere (about 380 ppmv) we need to account for an increase of about 36% from 1900 to now. This would be an increase of about 2.16×10^{17} g carbon. Thus, the lowered solubility of just the top 100 m, the well mixed layer of the ocean, is not sufficient to account for the increase in CO_2 in the atmosphere.

Next, if we calculate the carbon that would be available from the top 500 m of the ocean, we have a reservoir in this volume of seawater of about 3.74×10^{18} g carbon. Using the 0.726% decrease in CO_2 solubility we can calculate that the top 500 m would account for a total loss of 0.272×10^{17} g carbon due to the slow ocean warming. This is about 10% of the increase in the atmosphere that has actually been measured.

Finally if we include the entire DIC reservoir of the ocean, then the loss of carbon dioxide would amount to about 2.73×10^{17} g of carbon. This is just slightly greater than the increase

observed in the atmosphere since 1900. Thus we see that simple physical chemistry and slight changes in the model accounting for anthropogenic fossil fuel emissions removes the "mystery" of why only about half of the CO_2 appears to be dissolving in the ocean with about half remaining in the atmosphere and slowly increasing.

These calculations show that all of the anthropogenic fossil fuel gases are quickly removed from the atmosphere and dissolve in the ocean. It is the enthalpy of mixing of these fossil fuel emissions that accounts for the temperature rise in the ocean and of the pH decrease of the ocean (the strong acid gases only) in the last 50 to 60 years. Furthermore, it is the degassing of CO_2 from the warming oceans that is the cause of the steady rise in CO_2 measured in the atmosphere. Since the entire ocean DIC appears to be in equilibrium with the entire atmosphere over less than 100 day periods, this leads to an explanation for the hitherto very puzzling (to a chemist) fact that DIC concentration in the ocean is invariant with depth. Given the ocean's temperature gradient and very large pressure gradient a chemist would predict much higher DIC concentrations at the ocean bottom. The need to involve the entire ocean volume to account for solubility decrease equilibrium with the atmosphere explains this constant DIC with depth.

When we look for explanations of the warming effect of the atmosphere there is one simple physical effect caused by waste heating of the air by fossil fuel combustion that must first be calculated. If one calculates the heat energy increase of the atmosphere due simply to increasing waste heat emissions, and again using the weight of the atmosphere and its specific heat, one can generate a temperature increase of almost 3.0 ºC, which is 4 times the actual atmospheric average temperature rise measured over the last 60 years. This physical effect alone is similar to that of Arhennius' early 20th century calculation of Fourier's greenhouse gas hypothesis for warming the atmosphere. Regardless of the actual mechanism of atmospheric warming, the entire question is begged by the small contribution of atmospheric warming to the total warming of ocean and atmosphere. Since "global" warming must be defined as the sum of these two effects, then the explanation for the ocean warming of the top 1,000 meters is 170 times more important than an explanation for atmospheric warming.

The idea that CO_2 is the cause of atmospheric warming over geological time frames is also clearly wrong. Most geologists attribute the cause of global cooling and warming to the variation over geologic times of the earth's distance from the sun which effects the surface temperature on land and sea. This variation is caused by a combination of the eccentricity of the earth's orbit, the obliquity of the earth axis of rotation with its solar orbit, and the wobble of the axis of revolution (the cause of earth's precession). This idea was first postulated by Kroll in 1860 and later refined by Milankovitch in the early 20th century. This idea clearly explains the glacial and interglacial periods and calculations of the combination of these 3 effects over millions of years shows that the small temperature changes come first, followed by advance or retreat of glaciers and finally closely followed by changes in atmospheric CO_2. Just as in the very recent anthropogenic case above, in the geologic time frame case CO_2 is a marker for temperature change simply because of its increase or decrease in solubility in the ocean. As the ocean temperature falls, CO_2 concentration in the atmosphere falls and as ocean temperature warms, CO_2 degasses back to the atmosphere and its concentration there (and eventually in trapped ice cores, etc) increases.

17.2 Implications of the Above Ideas On The NRL Synfuel Project

The above alternative hypothesis has arisen because of the need to really understand what is going on from anthropogenic fossil fuel burning. The need to understand the real relationships between hydrocarbon burning and the fate of carbon dioxide is the NRL approach to alternative fuel substitutes for fossil fuels. Nuclear energy is seen as a mid range bridging technology to supply the electrical energy at sea necessary to capture carbon, produce hydrogen and ultimately to produce oil. Ultimately, the idea is to use ocean thermal energy conversion (OTEC) to produce fossil fuel free electricity in the equatorial belt of earth. Carbon dioxide (from the total dissolved inorganic carbonate system) will be recovered as a source of carbon at sea. The carbon and hydrogen will be chemically reacted to produce hydrocarbon fuel suitable for burning in current available engines. The question arises that if this process is scaled up to meet most naval needs for liquid hydrocarbons what would be the effect on the ocean, and what would be the effect on the atmosphere and on global warming? Beyond that, what is the answer to this question if ultimately increasing the use of this process in the future to include all US needs (approximately 300 times those of the USN) and even all world needs (approximately another 5 times beyond the US total needs)?

It is clear from early calculations that the ocean is fully capable of producing all the energy requirements on earth hundreds of times over by the process outlined above, OTEC plus CO_2 recovery from ocean bicarbonate. Because of the overwhelmingly large total DIC content of the ocean only about 100 parts per million per year would ever be used even if the process provided all sources of human energy to replace current fossil fuels. Of course, the process is cyclical and so is overall carbon neutral.

But given what we now know from the above discussion in Section 17.1, taking CO_2 from the ocean and converting it to hydrocarbon and then back to CO_2 in the atmosphere, will still continue to cyclically increase the heat content of the ocean. This is clearly very undesirable from an ecological point of view. So should we continue to develop and finally scale up this new alternative process? The answer lies in the fact that OTEC is a heat pump running in reverse to extract heat from the ocean and thus effectively lowering its temperature. Each 100 MW plant is capable of producing a minimum of 42,000 gallons of liquid hydrocarbon per day. When burned as a fuel this 294,000 lbs produces about 882,000 lbs of CO_2 per day which dissolves in the ocean (this time with no SO_X, so no more pH lowering). The enthalpy of mixing is about -19 kJ/moles. This amounts to 400×10^6 grams CO_2 divided by 44 g/mol which gives 9.1×10^6 moles per day. This is about 173,000,000 kJ/day of heat added to the ocean.

However, this is balanced by the extraction of heat from the ocean by OTEC. 100 MW per day is 2,400,000 kW hour which is 8,640,000 MJ per day, or $8,640 \times 10^9$ joules per day. The heat added per day by dissolving CO_2 from the fuel produced by this OTEC heat removal is about 173×10^9 J per day. Thus every day that a 100 MW unit process operates there is about 50 times more heat removed that added. Eventually, this process will start to cool the ocean over many years with full-scale global production involving up to 50,000 large vessels.

The net effect of the synthetic fuel scheme should be to greatly reduce (to zero) the particulate and sulfur emissions of energy production by combustion. The effect on the atmosphere will be a slow but steady reduction in CO_2 as the ocean begins to cool. The process itself will eventually cool the ocean at full scale global production and this will be very beneficial to all ocean life. The pH of the ocean will eventually re-equilibrate to pre-industrial levels due again to the zero sulfur content in the new alternative fuel. This also will be of immense biological benefit to the ocean. As the ocean slowly cools to its pre-industrial levels this should have an immense positive impact on global weather patterns. Arctic and Antarctic ice will slowly become reestablished. However, land glaciation will probably not be reversed. Given the potential future ocean temperature imbalances, it may be that OTEC will be restricted to only a fraction of total future world energy supply.

17.3   Whither Future Energy Research Within The Navy?

This report began with a history of fuel chemistry research within the Navy during most of the 20th century. In order to put into context any future alternative fuel research within the Navy in the coming century, several important factors must be understood. First, before the creation of the Department of Energy in 1976, each of the services maintained a large basic and applied program of current and future fuel research. After this time, the ONR and NRL made a conscious decision to let DOE take the lead in all future alternative fuel research, with the exception of one final large shale oil program that spanned a period from 1975 through 1985. During that program large amounts of supporting funding actually flowed from DOE to NRL and other Navy laboratories.

In an effort to respond to DOE and Executive orders to be more environmentally compliant or more energy efficient, the Navy is constantly seeking to be involved reactively in a host of schemes such as hydrogen, biofuels, and other non-renewable sources of energy that it clearly has only marginal interests in, instead of pursuing a course of action that has critical naval interest such as high temperature gas cooled (HTGC) nuclear reactors, ocean thermal energy conversion, carbon capture, and the current synfuel program from environmental sources of carbon and hydrogen. This is the result of the lack of an "honest broker" in the area of future alternative fuel for the Navy or indeed for the other services and DOD. There needs to be an acceptance that the DOE has not provided the military with anything that could be used as future energy sources in its 35 year history and that it is unlikely to do so at any time in the future.

The second factor is the long held belief within the Navy at all levels that there is no need for Navy involvement in future alternative fuel research beyond certain small niche areas of interest only to the Navy such as UUV power sources or remote station power sources. This belief is based on the seemingly inexhaustible source of crude oil for Navy energy needs for power and propulsion. Coupled to this is the belief that even if shortages occur in the future, naval needs will be met at the expense of civilian needs (as in WWII) or that our naval energy needs will be met by military force if necessary (again as in WWII). The inevitable fact of the inexorable increase in cost of energy (really very small when adjusted for inflation over the last 50 years) is not really of any concern to Navy energy policy planners, especially for future planning beyond several years.

The third factor, is the long held belief that the Navy's primary mission is one of projecting military power for the US and this is hard to dispute. The idea that the Navy might become a supplier of its own ammunition, platforms, food or fuel is seen as interfering with its primary mission. Again, the exception would be the Navy development of such specialty energy related items as thionyl chloride batteries.

Because of these 3 factors, the Navy has lacked any kind of long term vision of any potential large scale replacements for oil for the last 25 years and this has led to a vacuum in the Navy and, indeed in all of DOD (e.g., DARPA) of any expertise in this area. This is regardless of the nature of the energy effort, whether basic science or applied. All of these historical developments have conspired to the detriment of the current project which is simply the development of an extremely large Navy niche area – the production of power and propulsion fuel at sea. This project to date has largely been a bottom-up basic science approach but as it leaves its conception and infancy stages and heads on to adolescence it requires two things. First, it needs additional financial support, and second, it needs top-down support and commitment from the Navy Secretariat and the CNO Executive.

A vision of Navy air and sea propulsion fuel 30 years in the future might underscore the potential of this synfuel project. First suppose that the Navy synfuel program has progressed successfully past its adolescence and it is now 2020. Imagine that the Military Sealift Command has successfully designed and constructed 5 large HTGC reactor powered ships and 10 large OTEC ships. The HTGC ships are capable of producing 800 MW of power and each of the OTEC ships of 200 MW of electrical power for the production of synthetic hydrocarbon fuel. The HTGC conversion efficiency amounts to 800,000 gallons per day for each ship and the OTEC conversion amounts to about 150,000 gallons per day of finished fuel. This is a total daily production of about 5.5 million gallons. The Navy daily total usage is only about 4.5 million gallons and so the additional million gallons per day can go to supplying overseas AF and Army bases. The construction costs of the ships would be about $2 billion for each HTGC ship and about $0.5 billion for each OTEC ship. This would be a total cost of about $15 billion and each ship would have a life span of at least 30 operational years. The operating cost of all 15 ships would be about $1.5 billion yearly. The value of the fuel produced (at $3 per gallon comparable crude oil based fuel) would be about $6 billion per year. Over 30 years at constant cost and no inflation this would amount to $180 billion. The cost of storage and supply currently is estimated to be about $1.5 to $3.0 billion and this would be reduced to about $0.15 billion per year for the Navy alone.

Thus the Navy would save over a 30 year period a value of approximately $153 billion, or over $5 billion per year. The continued nurturing of this project as it now approaches 9 years since conception and birth is necessary in order to achieve these future potentials. Certainly this project like any given individual could run into insurmountable difficulties that would call a halt to its life at any time. Until that time, it is hoped that it will continue to mature and develop which requires continued support and funding.

18.0   REFERENCES

1. Strucko, R., Giannini, R., and Hardy, D. "Perspectives on US Naval Shipboard Fuels, Past, Present, and Future," Proc. of the ONR Conf. on Development of New Hot Section Materials for Gas Turbines, Col. School of Mines, Golden, CO, Oct. 3, 2002.
2. NRL Energy Research Panel "A Study of the Navy's Energy Research Needs from the Viewpoint of NRL Involvement," NRL Memo Report 3027, November 1974.
3. Avery, W. H., Wu, C. *Renewable Energy From The Ocean,* Oxford University Press: New York, 1994.
4. Hardy, D. R., Rath, B. B., Hurdle, B. G., Carhart, H. W., Coffey, T. and Saalfeld, F. E. "DOD Future Energy Resources," *Proceedings of Energy Workshops of 2002 and 2003*, National Defense University, Washington, DC, June 2004.
5. Carhart, H. W., Affens, W. A., Boss, B. D., Hazlet, R. N. and Schuldiner, S. "Hydrogen as a Navy Fuel," NRL Report 7754, June 12, 1974.
6. Coffey, T., Hardy, D. R., Besenbruch, G. E., Schultz, K. R., Brown, L. C. and Dahlburg, J. "Hydrogen as a Fuel for DOD," *Defense Horizons* 2003, *36*, 1.
7. Johnson, K. M., King, A. E., and Sieburth, J. M. "Coulometric TCO$_2$ Analyses for Marine Studies; An Introduction," *Marine Chemistry;* Elsevier Science Publishers: Amsterdam 1985.
8. Dorchak, D., Chang, S.G., Huang, H. "Method to Regenerate Ammonia for the Capture of Carbon Dioxide," *Energy & Fuels*, 2002, Vol. 16, 904-910.
9. Rautavouma, A., "The Hydrogenation of CO on Co Catalysts," 1979, http://www.fischer-tropsch.org/DOE/DOE_reports/rautavouma_thesis/rautavouma_toc.htm.
10. Lapidas, A. L. "The Mechanism of Carbon Dioxide Hydrogenation on Copper and Nickel Catalysts," *Petroleum Chemistry*, 47 (2) March 2007, 75-82.
11. Centi, G., Percthomer, S. and Rak, Z. "Gas phase electrocatalytic conversion of CO$_2$ to fuels over gas diffusion membranes containing Pt or Pd nanoclusters," *Studies in Surface Science and Catalysis*, 145 (2003) 283.
12. Olah G. A., Goeppert, A., Prakash, G.K.S. *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006.
13. Benson, E.E., Kubiak, C.P., Sathrum, A.J., Smieja, J. M. "Electrocatalytic and homogeneous approaches to conversion of carbon dioxide to liquid fuels," *Chem. Soc. Rev.,*2009, 38, 89-99.
14. Bogart, S. L., Schultz, K., Brown, L., and Russ, B. "Production of Liquid Synthetic Fuels from Carbon, Water and Nuclear Power on Ships," *International Conference on Advanced Power Plans*, Reno, Nevada, 7 June 2006.
15. Schultz, K., Bogart, S. L., Noceti, R. P. "Synthesis of Hydrocarbon Fuels Using Renewable and Nuclear Energy," *Topical Meeting on Safety and Technology of Nuclear Production of Hydrogen*, Boston, MA, 26 June 2007.
16. Hardy, D. H., Zagrobelny, M., Willauer, H. D., Williams, F. W. "Recovery of Carbon Dioxide from Seawater by Ion Exchange Resin Part I: Using a Strong Acid Cation Exchange Resin," NRL Memo Report 6180-07-9044, April 20, 2007.
17. Willauer, H. D., Hardy, D. R., Lewis, M. K., Ndubizu, E. J. and Williams, F.W. "Aqueous Bicarbonate Recovery from Seawater and Model Systems Using a Gas Permeable Membrane," NRL Memo Report, 6180-08-9129, 25 June 2008.

18. Willauer, H. D., Hardy, D.R., Lewis, K.M., Ndubizu, E.C. and Williams, F.W. "The Effects of Pressure on the Recovery of CO_2 by Phase Transition from a Seawater System by Means of Multi-layer Gas Permeable Membranes," *J. Phys. Chem. A,* 2010, 114, 4003-4008.

19. Willauer, H. D., Hardy, D. R., Lewis, M. K., Ndubizu, E. C. and Williams, F. W. "Recovery of CO_2 from Aqueous Bicarbonate Using a Gas Permeable Membrane," *Energy & Fuels*, 2009, *23*, 1770- 1774.

20. Mackenzie, F. T. and Lerman, A. *Carbon in the Geobiosphere – Topics in Geobiology, Vol. 25*, Springer, Dordrecht, The Netherlands, 2006.

19.0   ACKNOWLEDGEMENTS